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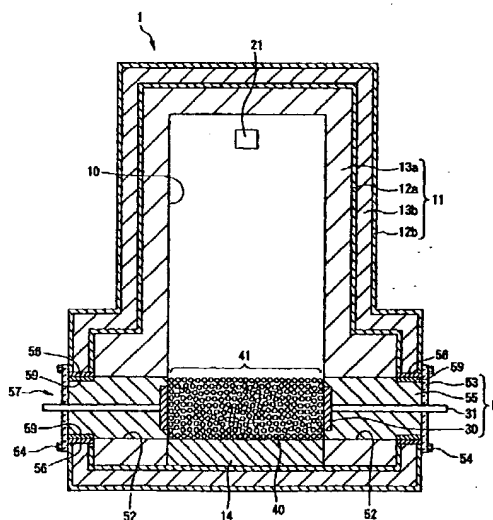
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(57) An inventive thermal decomposition apparatus for wastes comprises: a heating chamber for heating the wastes; an inlet port for introducing the wastes into heating chamber; at least one pair of electrodes provided within the heating chamber; a plurality of balls each taking the form of a sphere whose main ingredient is carbon, provided between the at least one pair of electrodes so as to produce an electric discharge when a voltage is applied across the at least one pair of electrodes; an outlet port for discharging out of the heating chamber gases into which the wastes are thermally decomposed; oxygenless or vacuum state forming means or evacuating means for placing the heating chamber in an oxygenless or vacuum state such that the balls are placed in an oxygenless state.

According to the present invention, an inexpensive thermal decomposition apparatus for wastes is provided which thermally decomposes almost all wastes at a high temperature of not lower than about 3000 °C without producing any harmful substances such as soot dust, chlorine compounds such as hydrogen chloride, nitrogen compounds such as NO<sub>x</sub> and/or dioxin.

FIG. 2



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## Description

## TECHNICAL FIELD

5 [0001] The present invention relates to thermal decomposition apparatus for thermally decomposing various wastes which contain general wastes including polymer ones of resins, industrial wastes, infectious medical wastes, and chemical substances such as PCB and waste oils without producing any gas containing harmful substances.

## BACKGROUND ART

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[0002] In the current society, an enormous amount of wastes are discharged daily and their disposal is a great problem. The wastes include various kinds of wastes such as general, industrial and medical ones. Most of them are processed by burning or burying them, which has several problems.

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[0003] The maximum problem with the burning process is that harmful substances are produced by burning the wastes. In the burning process, the wastes are burnt with fed air. Thus, harmful substances such as soot dust, carbon dioxide and nitrogen compound such as  $\text{NO}_x$  are produced, and discharged with other exhaust gas. Since the burning temperature is at about 700-800 °C, harmful dioxin would be necessarily produced more or less, and hence exhaust gas and ashes containing dioxin would be produced.

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[0004] The harmful substance content of the exhaust gas is regulated globally. Especially, dioxin has very high toxicity which adversely affects the human bodies for a long time and its discharge is strictly regulated.

[0005] In order to prevent production of dioxin, the following measures have been taken mainly:

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(1) The wastes which produce no dioxin are segregated from the ones which produce dioxin, and only the ones which produce no dioxin are burnt;

(2) A device for removing dioxin contained in the exhaust gas discharged from an incinerator is attached to an incinerator; and

(3) An incinerator which burns wastes at such a high temperature that dioxin is difficult to produce (hereinafter referred to as a high temperature incinerator) is used.

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[0006] There is, however, the problem with the above method (1) that it takes time and costs considerably to segregate the wastes. In addition, it is substantially impossible to perfectly separating the wastes, and production of a small amount of dioxin cannot be avoided.

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[0007] The above method (2) is insufficient to cope with dioxin because a device capable of completely removing dioxin is not put to practical use at present. Thus, it is insufficient to cope with dioxin. Thus, a secondary incinerator for burning dioxin contained in the exhaust gas, a cooling device for rapidly cooling the exhaust gas so as not to reproduce dioxin, and a bug filter for removing dioxin remaining in the exhaust gas are installed very often in the incinerator. However, installation of such devices in combination requires a high cost and renders the incinerator complicated.

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[0008] As described above, the exhaust gas contains a plurality of harmful substances in addition to dioxin. In order to eliminate them all, a plurality of devices for removing such harmful substances are required to be attached to the incinerator. Thus, the incinerator would become expensive and complicated in composition.

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[0009] Since the high temperature incinerator is expensive, there is the problem with the above method (3) that it is not easy to destroy the old incinerator and to newly build up a high temperature incinerator. In addition, it is difficult to completely prevent production of even a small amount of dioxin even if the high temperature incinerator which is put to practical use at present is used.

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[0010] Burning the wastes also has problems other than production of the harmful substances. Usually, wastes contain incombustible substances such as metals and glass. Therefore, when the wastes are burnt as they are, incombustible dregs are produced and required to be removed from the incinerator, which takes much time. In terms of time and cost, it is difficult to segregate the wastes according to material and then to process them separately.

[0011] In addition, there are wastes, most of which contain incombustible materials such as industrial wastes and shredder dust including pieces into which car bodies and household electric appliances are broken. Those wastes are not suitable for burning.

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[0012] The other method for processing the wastes is to bury them. Now, it is, however, difficult to secure a place where the wastes are to be buried. In addition, there is the problem that chemical substances contained in the wastes will react in the earth to resynthesize new chemical (harmful) substances. Furthermore, harmful heavy metals such as lead and/or harmful chemical substances such as dioxin contained in the wastes dissolve in rain to pollute soil, rivers and ground water (soil pollution, water pollution) to thereby destroy the environment greatly.

[0013] Methods appropriate (efficient and safe) to dispose of certain ones of the wastes such as PCB and/or dioxin

are not yet found, and hence those wastes can only be stored and kept. Such wastes may leak out during their storage to pollute the environment and hence straightaway measures are required to be taken.

[0014] In order to solve the above various problems, apparatus capable of disposing of all wastes without producing harmful substances have been demanded, for example, apparatus for thermally decomposing the wastes at high temperatures without burning them. However, it is difficult to efficiently obtain high temperatures to thermally decompose all the wastes. Thus, those apparatus have not been put to practical use at present.

[0015] It is therefore an object of the present invention to provide inexpensive thermal decomposition apparatus for wastes which solves the above problems and which thermally decomposes almost all wastes without producing harmful substances such as soot dust, chlorine compounds such as hydrogen chloride, nitrogen compounds such as  $\text{NO}_x$  and/or dioxin.

#### DISCLOSURE OF THE INVENTION

[0016] In order to achieve the above object, the present invention provides a heating chamber for heating wastes, an inlet port for introducing the wastes into the heating chamber, at least one pair of electrodes provided within the heating chamber, a light emitting heater consisting of a plurality of balls which contain carbon as a main ingredient, the light emitting heater being provided between the at least one pair of electrodes so as to produce an electric discharge when a voltage is applied across the at least one pair of electrodes, and an outlet port for discharging out of the heating chamber gases into which the wastes are thermally decomposed.

[0017] In the arrangement, electric discharges occur between the plurality of balls. Since the electric discharges occur at a high temperature of about 3000 °C, almost all wastes including PCB except for metals having high melting points are thermally decomposed at such high temperatures into harmless low molecular-weight substances without producing any harmful substances such as dioxin.

[0018] Thus, even wastes containing incombustible wastes which cannot be disposed of in the general burning method can be thermally decomposed simultaneously without being separated or segregated. Even when the wastes which may produce dioxin in the burning process are contained, they are thermally decomposed without being segregated. Thus, much time and cost are not required for disposing of the wastes.

[0019] After the thermal decomposition, few dregs are produced and no work for removing such dregs is required.

[0020] The remainder of the burned wastes containing dioxin produced by burning the wastes, and wastes such as PCB whose processing methods have not been found and which have only been stored and kept are thermally decomposed similarly into harmless low molecular-weight substances.

[0021] As described above, the present invention is realized by generating an extremely high temperature of about 3000 °C efficiently in a stabilized manner and by maintaining its temperature.

[0022] The electric discharging region is at a high temperature of about 3000 °C and a position distant ten-odd centimeters from the discharging region is at about 200 °C or less. Thus, the inner and outer walls of the thermal decomposition apparatus is capable of sufficiently keeping a high temperature of about 3000 °C even they have a simple structure. Thus, such apparatus has a simple structure and is made inexpensively.

[0023] The low molecular-weight substances produced by the thermal decomposition are rapidly cooled from about 3000 °C to about 200 °C or less to thereby eliminate the probability of dioxin being reproduced. If they are cooled gradually, they are placed for a long time at a temperature where dioxin is likely to produce.

[0024] The thermal decomposition apparatus preferably comprises oxygenless state forming means for placing the heating chamber in an oxygenless state such that the plurality of balls are placed in an oxygenless state. Thus, the plurality of balls are difficult to oxidize, deteriorate, and deform to decrease in discharge efficiency, and are usable for a long time. For example, when the plurality of balls each take the form of a perfect sphere, they provide a very high discharging efficiency, whereas when they are deformed due to their oxidization and deterioration, the discharging efficiency can decrease. The oxygenless state in the present invention implies that the oxygen concentration is lower than that in air.

[0025] As the oxygen concentration becomes lower, it is more preferable. If it is lower than that in air, there is no problem. When the oxygen concentration exceeds that in air, the plurality of balls are liable to be oxidized and deteriorated.

[0026] The apparatus preferably comprises decompressing means for decompressing the heating chamber such that the plurality of balls are placed in a vacuum state. In this case, a high discharging efficiency and a high temperature are easily obtained. In addition, a high temperature is obtained with small power to thereby reduce the operating cost of the apparatus. Like the case where the plurality of balls are placed in the oxygenless state, they are difficult to deteriorate and usable for a long time. Since the density of molecules present in the vacuum state is low, new chemical substances are difficult to produce due to recombination of decomposed molecules, advantageously. The vacuum state in the present invention implies that the vacuum degree is less than the atmospheric pressure.

[0027] As the vacuum degree becomes higher, it is more preferable. A medium vacuum ( $10^{-2}$  or more and less than

10 Pa) will suffice. It may be a lower vacuum (10 Pa or more and less than the atmospheric pressure).

[0028] The plurality of balls may be each made of at least one selected from the group of charcoal, graphite and a carbon composite material. As an example of charcoal, Japanese Bincho charcoal can be named. Carbon such as charcoal and graphite has many pores on its surface and in its inside in which a gas is adsorbed. Thus, there is the problem that at high temperature the adsorbed gas will be discharged. Thus, it is preferable to process carbon such as charcoal and/or graphite such that their pores are closed to prevent adsorption of a gas.

[0029] The plurality of balls each have impermeability preferably. In that case, their substance absorptivity is low to thereby decrease the probability that they will adsorb or release harmful substances in use. Thus, since they are difficult to deteriorate with oxidization and harmful chemical substances, they are usable for a long time.

[0030] It is preferable that the plurality of balls each take the form of a sphere. In order to cause electric discharges efficiently between the plurality of balls, they are preferably in point contact, one with another. If they are in line or surface contact, one with another, many undesirable great flows of electric currents would occur to thereby reduce the discharge efficiency. Thus, when they are each in the form of a sphere, they are necessarily in point contact, one with another, the discharges are performed efficiently, a high temperature is easily obtained, and the operating cost of the apparatus is reduced.

[0031] The use of the plurality of balls for a long time deteriorates themselves due to the discharges and oxidization to thereby deform them possibly. Especially, when the electric discharges concentrate on particular part of the balls, the particular part are liable to deteriorate greatly. If the plurality of balls each take the form of a sphere, they rotate due to the action of the electric discharges. Thus, the electric discharges are difficult to concentrate on the particular part and there is a high probability that the electric discharges will occur uniformly among all part of them. Thus, even when they are deteriorated and/or deformed, they are kept in the form of a sphere, and the probability that the electric discharge efficiency will be reduced is low, advantageously.

[0032] As long as the plurality of balls are placed in point contact, one with another, they may each take the form of a polyhedron such as a dodecahedron or icosahedron. The term "sphere" used in the present invention should include a true sphere as well as a polyhedron. The plurality of balls each take the form of a perfect sphere preferably.

[0033] Pressing means for pressing the wastes against the plurality of balls may be provided within the heating chamber.

[0034] By this arrangement, the wastes are placed in efficient contact with the discharging portions of the plurality of balls. Thus, the wastes are heated efficiently at a temperature, for example, of about 3000 °C to thereby improve the heat decomposing efficiency of the wastes.

[0035] The apparatus may further comprise a filter made of at least one of activate carbon and charcoal for allowing the decomposed gases to pass therethrough.

[0036] In this case, even when the decomposed gases contain hydrocarbons, heavy metals and/or undecomposed harmful substances, the filter will adsorb them to prevent them from being discharged out of the apparatus.

[0037] The apparatus may further comprise a vacuum meter for measuring the pressure within the heating chamber, and pressure adjusting means for adjusting the pressure within the heating chamber to a predetermined value.

[0038] In this arrangement, the inside of the heating chamber is automatically adjusted to an optimal pressure.

[0039] The apparatus may further comprise an intervening spacer which contain carbon as a main ingredient, the intervening spacer being placed between the plurality of balls and an inner wall of the heating chamber. Since in this arrangement the inner wall of the heating chamber is not contact with the plurality of balls of high temperatures, the former is difficult to deteriorate with heat to thereby improve the durability of the inner wall.

[0040] The intervening spacer may be made of a carbon material such as impermeability graphite, and its shape is not especially limited and may take the form of a plate or rod.

[0041] At least portions of the inner wall of the heating chamber which are placed in contact with the plurality of balls may be made of a monolithic refractory which contains at least one selected from the group of boron nitride (BN), niobium (Nb), silicon carbide (SiC), boron carbide ( $B_xC_y$ ), magnesium oxide (MgO), hafnium oxide (HfO), hafnium dioxide ( $HfO_2$ ), and beryllium aluminum oxide ( $Al_2BeO_4$ ,  $BeO \cdot Al_2O_3$ ). In this arrangement, the monolithic refractory has high thermal resistance which resists a high temperature of about 3000 °C. Thus, the inner wall of the heating chamber is rarely deteriorated.

[0042] Especially, since the boron nitride has a high melting point of 3000 °C, the monolithic refractory containing this material is excellent in thermal resistance, and the inner wall of the heating chamber is rarely deteriorated or melted due to heat. The inner wall of the heating chamber has high electric insulation resistance at high temperature, and no electric current flows through points where the inner wall of the heating chamber is in contact with the plurality of balls.

[0043] Addition of niobium and/or silicon carbide to the monolithic refractory improves its strength at high temperatures. Boron carbide includes various compounds of two ingredients. Monolithic refractories containing such compound have a low density and a higher strength. Monolithic refractories containing hafnium oxide exhibit excellent corrosion resistance. Monolithic refractories containing magnesium oxide exhibit excellent heat and fire resistance.

[0044] At least a part of the at least one pair of electrodes may take the form of a rod or horn surrounded by the

plurality of balls to thereby improve the discharge efficiency.

[0045] The apparatus may further comprise a pipe for introducing liquid wastes into the heating chamber.

[0046] The thermal decomposition apparatus may further comprise a decomposed gas harm eliminating device for thermally decomposing harmful materials remaining in the decomposed gases into harmless gases. The decomposed gas harm eliminating device may comprise: a decomposed gas heating chamber for heating the decomposed gases; a decomposed gas inlet port for introducing the decomposed gases into a decomposed gas heating chamber; at least one pair of second electrodes provided within the decomposed gas heating chamber; a second light emitting heater consisting of a plurality of second balls which contain carbon as a main ingredient, the second light emitting heater being provided between the at least one pair of second electrodes so as to produce an electric discharge when a voltage is applied across the at least one pair of second electrodes; a harmless gas outlet port for discharging out of the decomposed gas heating chamber harmless gases to which the decomposed gases are changed; and a filter comprising at least one of active carbon and charcoal for allowing the harmless gases to pass therethrough.

[0047] In such arrangement, electric discharges occur between the plurality of second balls of the device. The discharging regions are at a high temperature of about 3000 °C. Thus, even when the decomposed gases contain hydrocarbon compounds and/or harmful substances, the device thermally decomposes them completely to make them harmless. Thus, there is substantially no probability that the harmful substances will be discharged out of the apparatus.

[0048] The decomposed gas harm eliminating device may further comprises at least one of a second vacuum meter for measuring the pressure within the decomposed gas heating chamber, and second pressure adjusting means for adjusting the pressure within the decomposed gas heating chamber to a predetermined value; a second intervening spacer which contain carbon as a main ingredient, the spacer being placed at least between the plurality of second balls and an inner wall of the decomposed gas heating chamber; at least portions of the inner wall of the decomposed gas heating chamber which are placed in contact with the plurality of second balls being made of a monolithic refractory which contains at least one selected from the group of boron nitride, niobium, silicon carbide, boron carbide, magnesium oxide, hafnium oxide, hafnium dioxide, and beryllium aluminum oxide; and a second pair of electrodes having at least a part thereof in the form of a rod or horn surrounded by the plurality of second balls.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0049]

FIG. 1 is a perspective view of a thermal decomposition apparatus for wastes as a first embodiment.

FIG. 2 is a cross-sectional view of the thermal decomposition apparatus taken along a line A-A of FIG. 1.

FIG. 3 is a cross-sectional view of the thermal decomposition apparatus taken along a line B-B of FIG. 1.

FIG. 4 schematically illustrates electric discharges occurring among the plurality of balls.

FIG. 5 is a vertical cross-sectional view of a modification of the first embodiment.

FIG. 6 is a horizontal cross-sectional view of a modification of the first embodiment.

FIG. 7 is a cross-sectional view of a thermal decomposition apparatus for wastes as a second embodiment.

FIG. 8 is a cross-sectional view of the thermal decomposition apparatus taken along a line C-C of FIG. 7.

FIG. 9 is a perspective view of a thermal decomposition apparatus for wastes as a third embodiment.

FIG. 10 is a partial horizontal cross-sectional view of the thermal decomposition apparatus of FIG. 9.

FIG. 11 is a vertical cross-sectional view of a thermal decomposition apparatus for wastes as a fourth embodiment.

FIG. 12 is a cross-sectional view of the thermal decomposition apparatus taken along a line D-D of FIG. 11.

FIG. 13 is a vertical cross-sectional view of a thermal decomposition apparatus for wastes as a fifth embodiment.

FIG. 14 shows a vertical cross-sectional view and a horizontal cross-sectional view of a lower portion of a heating chamber of a thermal decomposition apparatus for wastes as a sixth embodiment.

FIG. 15 is a vertical cross-sectional view of a thermal decomposition apparatus for wastes as a seventh embodiment.

FIG. 16 is a perspective view of a mount for the light emitting heater unit.

FIG. 17 shows a side view and a plan view of the mount to which intervening spacers are fixed.

FIG. 18 is a perspective view of a carbon electrode to which a pair of spaced horn electrodes are attached.

#### BEST MODE FOR CARRYING OUT THE INVENTION

[0050] Embodiments of the thermal decomposition furnace according to the present invention will be described in more detail with reference to the accompanying drawings. The terms indicating directions such as "up", "down", "front", "rear", "right" and "left" represent respective directions in each of the drawings for convenience of explanation.

[0051] It is to be noted that the present invention is not limited to the embodiments described below.

(First Embodiment)

[0052] FIG. 1 is a perspective view of a thermal decomposition apparatus for wastes as the first embodiment. FIG. 2 is a cross-sectional view taken along a line A-A of FIG. 1. FIG. 3 is a cross-sectional view taken along a line B-B of FIG. 1.

[0053] The apparatus 1 includes an internal heating chamber 10 with an inlet port 20 on its front (on the left side thereof in FIG. 3) through which the wastes are introduced into the heating chamber 10 and an outlet port 21 on its rear (on the right side thereof in FIG. 3) through which the resulting thermally decomposed wastes are discharged from the heating chamber 10. The inlet port 20 has an operable door 22 such that when closed the airtightness of the heating chamber 10 is maintained.

[0054] The thermal decomposition apparatus 1 has an outer wall 11 of a 4-layered structure composed of an innermost refractory concrete layer 13a, an inner iron plate 12a, an outer refractory concrete layer 13b and an outermost iron plate 12b coated with a heat resisting coating. A portion of the innermost refractory concrete layer 13a positioned under a plurality of balls 40 in the form of a sphere is replaced with a heat-resisting firebrick layer 14 whose joints are filled with a monolithic refractory such as refractory concrete (not shown) to improve the airtightness of the heating chamber 10.

[0055] The inside of the heating chamber 10 is heated to a high temperature of about 3000 °C, as will be described later. However, a temperature at a position distant from scores of centimeters from a plurality of balls 40 is at a temperature of not higher than 200 °C and the inside of the heating chamber 10 is in an oxygenless or vacuum state. Thus, heat conduction is hardly performed and such a simple structure will suffice for the outer wall 11.

[0056] The rectangular parallelepiped space surrounded by a refractory concrete layer 13a forms the airtight heating chamber 10 where the wastes introduced through the inlet port 20 are heated and thermally decomposed, and the resulting gases are discharged from the outlet port 21.

[0057] The heating chamber 10 is filled in its lower portion with a plurality of balls 40 of carbon such as graphite. A light emitting heater 41 consists of a plurality of balls 40. Since the plurality of balls 40 each take the form of a sphere, adjacent ones of them are in point contact with each other. The composition of the balls 40 and a method of making them will be described in detail later.

[0058] A pair of plate-like carbon electrodes 30 are each disposed on a respective one of opposite sides a lower portion of the heating chamber 10 such that the plurality of balls 40 are disposed between the pair of carbon electrodes 30 from which a corresponding pair of carbon rods 31 outward extend respectively through the corresponding outer walls 11 of the apparatus 1. Each carbon rods 31 may be replaced with a heat-resisting refractory stainless steel one. It is to be noted that when the apparatus 1 has a structure in which the pair of stainless steel rods extend through the corresponding pair of carbon electrodes 30 to come into contact with the plurality of balls 40, the portions of the pair of stainless steel rods which comes into contact with the plurality of balls 40 should be covered by a carbon material to prevent deterioration thereof.

[0059] The outlet port 21 fluid communicates with a vacuum pump 51 through an exhaust pipe 23. The vacuum pump 51 corresponds to means for producing an oxygenless state or decompressing means as an element of the present invention. A vacuum meter and pressure adjusting means (not shown) are provided within the exhaust pipe 23. The pressure within the heating chamber 10 is measured by the vacuum meter. When the pressure measured by the vacuum meter exceeds a predetermined value, an excess gas is automatically adjusted (discharged) by the pressure adjusting means to thereby maintain the pressure within the heating chamber 10 at a constant value. In order that the heating chamber 10 is placed at the oxygenless or vacuum state, any means may be used as the oxygenless state producing means or decompressing means.

[0060] A fiber-like active carbon filter 50 is provided within the exhaust pipe 23. The active carbon has on its surface innumerable open pores which include micro ones having a diameter of not more than 2 nm, medium ones having a diameter of more than 2 nm and less than 100 nm, and macro ones having a diameter of not less than 100 nm, and has a specific surface area of 500-1700 m<sup>2</sup>/g. Thus, the active carbon has a strong absorptivity to selectively adsorb relatively large molecules physically, wherein the pores of various sizes adsorb various molecules. Especially, the active carbon is excellent in absorbing hydrocarbon such as methane. Instead of the fiber-like active carbon filter 50, particulate active carbon may be used as the filter. A filter of a material other than carbon may be used as long as it has excellent absorbability.

[0061] A pair of openings 52 each are provided axially outside a respective one of the pair of carbon electrodes 30 through a corresponding one of the opposite sides of the apparatus 1 so that inspection/maintenance of the inside of the apparatus 1 (including inspection of a deterioration in the quality, and replacement, of the balls 40 and carbon electrodes 30).

[0062] Each opening 52 is covered with an ceramic plate 53, which is removably fixed by bolts 54 to the outer wall 11. A refractory sealing sheet (not shown) is provided between each cover 53 and a corresponding one of opposite surfaces of the iron plate 12b of the outer wall 11 to provide satisfactory inside airtightness for the apparatus 1. A

refractory concrete block 55 is filled between each carbon electrode 30 and a corresponding cover 53 to provide satisfactory maintenance of the temperature within the apparatus 1. The cover 53 may be an iron plate covered with an insulating material. The refractory concrete block 55 may be replaced with a firebrick.

[0063] The four members, i.e., the cover 53, refractory concrete block 55, carbon electrode 30 and carbon rod 31, form an united electrode unit 57. Thus, the cover 53, refractory concrete block 55, carbon electrode 30 and carbon rod 31 are not required to be removed individually to replace the carbon electrode 30 with a new one. Instead, the electrode unit 57 is only required to be replaced wholly with another one to thereby facilitate replacing the carbon electrode 30 with a corresponding new one.

[0064] An outer rectangular iron frame 56 is provided so as to fit fixedly into an inner edge of each opening 52. A corresponding inner rectangular iron frame 59 is received within the corresponding rectangular iron cylindrical frame 56 so as to fit fixedly over a corresponding end portion of the refractory concrete block 13 for covering purposes such that the iron frame 59 slides along with the electrode unit 57 relative to the frame 56 to move the electrode unit 57 into/out of the opening 52.

[0065] A method of thermally decomposing the wastes, using such decomposing apparatus 1, will be described in detail next.

[0066] First, the door 22 of the inlet port 20 for the decomposition apparatus is opened, the wastes (not shown) are cast into the apparatus so as to be placed on the plurality of balls 40.

[0067] The vacuum pump 51 is then actuated to evacuate the heating chamber 10 into a vacuum state (for example, a high vacuum of about  $6.7 \times 10^{-2}$  Pa or a lower vacuum of about 0.02-0.06 MPa). Thus, the plurality of balls 40 filled into the heating chamber 10 are also placed in the vacuum state.

[0068] The pair of carbon rods 31 are connected to a power supply (not shown). When the pair of carbon electrodes 30 are impressed with a voltage of about 200 V (a current of 300-400 A), electric discharges occur among the balls 40 within the chamber 10. Electric discharges occur in the whole of the light emitting heater 41. In order to increase the discharge power, the pair of carbon electrodes 30 are required to be supplied with a voltage of 400-500 V (a current of 100-150 A).

[0069] The mechanism of occurrence of the electric discharges will be described with reference to FIG. 4. FIG. 4 (a) shows three balls 40 placed in contact with each other. FIG. 5 (b) illustrates the contacting portions of any two of the balls 40 in an enlarged view.

[0070] Since the plurality of balls 40 each take the form of a sphere, any adjacent ones thereof are in point contact with each other. Each balls 40 has a rugged surface microscopically. Thus, any adjacent balls 40 have microscopical convexities in contact with each other and concavities between the convexities on this surfaces. When a voltage is applied across the pair of electrodes, electric currents flow through points at which any two balls 40 are in contact with each other. However, the areas of the contact points are small and large currents cannot flow through the contact points, and electric discharges 42 occur across the concavities on the surfaces of the adjacent balls. When the balls 40 are in line/surface contact with each other to thereby provide large contact areas, large currents would flow through the areas and the discharge efficiency is reduced.

[0071] The discharge region (at spark 42) is at a temperature of about 3000 °C and the environment of the plurality of balls 40 is stabilized at a high temperature of 3000 °C in a short time of scores of seconds after a voltage is applied across the pair of carbon electrodes. At this time, the outer wall 11 (iron plate 12b) of the decomposition apparatus 1 is at about room temperature. If the electric discharges occur in a stabilized state, a low voltage of about 30 V (a current of 300-400 A) will suffice for the voltage to be applied. The resulting temperature may be adjustable depending on the applied voltage, as requested.

[0072] The use of the plurality of balls 40 for a long time deteriorates themselves due to the discharges and oxidation to thereby deform them possibly. Especially, when the electric discharges concentrate on particular parts of the balls 40, the balls 40 are liable to deteriorate greatly. Since the plurality of balls 40 each take the form of a sphere, they rotate due to the action of the electric discharges. Thus, the electric discharges are difficult to concentrate on the particular parts of the balls 40 and there is a high probability that the electric discharges will occur uniformly among whole of them. Thus, even when they are deteriorated and/or deformed, they are kept in the form of a sphere, and the probability that the electric discharge efficiency will be reduced is low, advantageously.

[0073] The wastes placed on the plurality of balls 40 are not burnt but heated to a high temperature of about 3000 °C to be thermally decomposed into harmless gases of low molecular-weight substances without producing harmful substances such as soot-dust, chlorine compounds such as hydrogen chloride, nitrogen compounds such as  $\text{NO}_x$ , and harmful substances such as dioxin. If such harmful substances are contained in the wastes, they are similarly decomposed thermally at the high temperature into gases of harmless low molecular weight substances.

[0074] Almost all wastes including powder/solid PCB except for metals having high boiling points are thermally decomposed at the high temperature of about 3000 °C. In that case, few dregs remain. Thus, incombustible wastes including glass articles such as bottles and metal articles such as cans, industrial wastes, medical wastes and shredder dust are thermally decomposed simultaneously without being segregated, not to mention general wastes such as

kitchen garbage and resins. When glass articles such as bottles are broken into pieces of substantially the same size as the balls 40, they come easily into contact with the balls 40 to thereby improve the thermal decomposition speed. Formless wastes are temporarily hardened to a lump having a fixed shape, for example, by compression and then broken into pieces to thereby improve the thermal decomposition speed similarly.

**[0075]** The electric discharges produce heat and light. The light is considered to be effective in expediting the thermal decomposition of the harmful substances. Especially, when dioxin is thermally decomposed, the effect of this thermal decomposition is considered to be high.

**[0076]** The decomposed gases can contain harmless low molecular weight substances as well as hydrocarbon and heavy metals, and are adsorbed by the active carbon filter 50. Thus, they are not discharged from the outlet port 21 of the apparatus 1. A very small amount of harmful substances can remain, but is adsorbed by the filter 50. Thus, no such gas is discharged from the outlet port 21 of the apparatus 1.

**[0077]** The filter 50 is restored repeatedly with water vapor of 120-200 °C sprayed thereagainst for reuse. Thus, this filter is excellent both in economy and prevention of secondary pollution. When a proportion of heavy metals adsorbed by the filter 50 increases, the heavy metals and other materials can be removed from the filter 50, crushed to pieces with an industrial mill and sifted according to specific gravity to collect the heavy metals.

**[0078]** As long as the object of the present invention is achieved, the positions of the inlet port 20, outlet port 21, vacuum pump 51 and the pressure adjusting device relative to the apparatus 1 are not limited to those of the present embodiment. For example, while the vacuum pump 51 is illustrated as being provided outside the apparatus 1 in the present embodiment, it may be provided within the apparatus 1.

**[0079]** While in the present embodiment the wastes are illustrated as being thermally decomposed in a state where they are placed on the plurality of balls 40, it is preferable that when the wastes are pressed against the plurality of balls 40, for example, by a spring or a weight placed on the wastes, a percentage of the wastes coming into contact with the plurality of balls 40 increases to thereby increase the thermal decomposition speed of the wastes.

**[0080]** FIGS. 5 and 6 show a modification of the first embodiment which comprises pressing means for pressing the wastes against the plurality of balls 40. FIG. 5 is a vertical cross-sectional view of the thermal decomposition apparatus 1a of the modification. FIG. 6 is a horizontal cross-sectional view of the thermal decomposition apparatus 1a. In FIGS. 5 and 6, the same reference numeral as that used in FIGS. 1-4 is used to denote the same element as, or an element corresponding to, that of the thermal decomposition apparatus 1 of the first embodiment.

**[0081]** Further description of elements of the thermal decomposition apparatus 1a of the modification identical or corresponding to ones of the thermal decomposition apparatus 1 of the first embodiment will be omitted and only elements of the modification different from those of the thermal decomposition apparatus 1 of the first embodiment will be explained next.

**[0082]** A pressure plate 61 which presses the wastes 60 against the plurality of balls 40 due to its own weight is suspended in a horizontal state by a rope 62 within the heating chamber 10. The rope 62 separates halfway into four subrope portions fixed to the respective corners of the pressure plate 61 such that the pressure plate 61 can easily take a horizontal attitude.

**[0083]** The rope 62 is connected at an upper end to an elevator 64 attached to the top of the thermal decomposition apparatus 1a such that the elevator 64 feeds out or rewinds the rope 62 to elevate and lower the pressure plate 61 within the heating chamber 10.

**[0084]** The heating chamber 10 has a pair of grooves 66 each provided on a respective one of opposite inner walls thereof and receiving slidably a respective one of a pair of horizontal projections 68 each provided at a respective one of opposite sides of the pressure plate 61 such that the pressure plate 61 move up and down along the pair of grooves 66 in the opposite inner walls in a stabilized manner.

**[0085]** By the pressing means which comprises such pressure plate 61, rope 62 and elevator 64, the pressure plate 61 is lowered depending on a degree of decomposition of the wastes 60 (a decomposed size of the wastes 60). Thus, the wastes 60 can be pressed against the plurality of balls 40 to maintain an efficient contact state at all times to thereby improve the decomposing speed of the wastes 60, which can be improved by about 30-40 % depending on the weight of the pressure plate 61, the kind of wastes 60 and the degree of vacuum.

**[0086]** Although the rope 62 is connected to the elevator 64 through the outer wall 11 of the decomposition apparatus 1a, the airtightness of the heating chamber 10 is sufficiently maintained.

**[0087]** The material of the pressure plate 61 is not limited as long as it has a sufficient weight, heat resistance and corrosion resistance. The material of the rope 62 is not especially limited as long as it has sufficient strength, heat resistance and corrosion resistance. The materials of the pressure plate 61 and rope 62 preferably include carbon, impermeability graphite, ceramic or heat-resisting stainless steel. The elevator 64 may be of the electrically or manually actuated type.

**[0088]** While in the modification the pressing means which presses the wastes 60 against the plurality of balls 40 with the weight of the pressure plate 61 is employed, pressing means may be employed which presses the wastes 60 against the plurality of balls 40 with a spring.



## (Second Embodiment)

**[0089]** FIG. 7 is a vertical cross-sectional view of a thermal decomposition apparatus 2 for wastes in the second embodiment. FIG. 8 is a horizontal cross-sectional view taken along a line C-C in FIG. 7. The same reference numeral is used to denote the identical or similar elements of the second and first embodiments in FIGS. 7, 8 and 1-4.

**[0090]** The thermal decomposition apparatus 2 of the second embodiment has an inlet port 20 suitable for introducing liquid wastes such as waste oils, waste liquids and/or PCB into the heating chamber, and is suitable for disposing of such liquid-like wastes. Further description of elements of the thermal decomposition apparatus 2 of the second embodiment identical or similar to those of the thermal decomposition apparatus 1 of the first embodiment will be omitted and only elements of the second embodiment different from those of the first embodiment will be explained next.

**[0091]** An inlet pipe 24 extends into the heating chamber 10 through a side wall of the decomposition apparatus 2 for feeding the liquid wastes into the heating chamber. The inlet pipe 24 separates into a plurality of subpipes (two in FIG. 8) and then merges into a single second pipe which is terminated and fixed in the inner wall of the heating chamber 10 opposite to the side wall of the heating chamber 10 through which the inlet pipe 24 passes.

**[0092]** The subpipes placed within the heating chamber 10 each have a plurality of holes 26 arranged through its length on its lower surface such that the liquid wastes 28 flowing through the inlet pipe 24 are discharged in the form of a shower, as the case may be, from the plurality of holes 26 against the plurality of balls 40. The inlet port 20 suitable for introducing liquid wastes is composed of the inlet pipe 24 and its holes 26.

**[0093]** The shape of portions of the inlet tube 24 within the heating chamber 10 is not especially limited, but is freely designable. While in the present embodiment the inlet pipe 24 is illustrated as being separated into the subpipes which then merge into one, it may be a non-divergent one or a divergent and non-merging one.

**[0094]** The material of the inlet pipe 24 is not especially limited as long as it has heat resistance and corrosion resistance to liquid wastes. Preferably, the material of the inlet pipe 24 include, for example, carbon, impermeability graphite, ceramic or heat resistance stainless steel.

**[0095]** A method of thermally decomposing the liquid wastes using the thermal decomposition apparatus 2 is similar to that used in the case of the first embodiment and further description thereof will be omitted.

## (Third Embodiment)

**[0096]** FIG. 9 is a perspective view of a thermal decomposition apparatus 3 for wastes as a third embodiment. FIG. 10 is a horizontal cross-sectional view of a part (a decomposed gas harm eliminating device 3b) of the thermal decomposition apparatus 3.

**[0097]** The thermal decomposition apparatus 3 as the third embodiment comprises a thermally decomposing device 3a and a decomposed gas harm eliminating device 3b connected to the thermal decomposing device 3a. The thermal decomposing device 3a thermally decomposes the wastes. The decomposed gas harm eliminating device 3b heats to a high temperature gases produced by thermal decomposition of the wastes in the thermal decomposing device 3a to thermally decompose harmful substances remaining possibly in the decomposed gases to thereby render the decomposed gases harmless.

**[0098]** The thermally decomposing device 3a is identical to the thermal decomposition apparatus 1 of the first embodiment except that the former lacks a filter such as that shown by 50 and a vacuum pump such as that shown by 51 and therefore the composition of the decomposed gas harm eliminating device 3b alone will be described below. In the present embodiment, the same element as, or an element corresponding to, that of the thermal decomposition apparatus 1 of the first embodiment is identified by the same reference numeral as was used in the first embodiment. The thermally decomposing device 3a may be replaced with the thermal decomposition apparatus 2 of the second embodiment.

**[0099]** The decomposed gas harm eliminating device 3b which inside includes a decomposed gas heating chamber 110 has a decomposed gas inlet port 120 on its front for introducing the decomposed gases into the heating chamber 110 and a harmless gas outlet port 121 on its rear for discharging the harmless decomposed gases out of the heating chamber 110. The outlet port 21 of the thermally decomposing device 3a fluid communicates through a connecting pipe 101 with the inlet port 120 of the decomposed gas harm eliminating device 3b. A vacuum pump 151 fluid communicates with the outlet port 121 through a discharge pipe 123.

**[0100]** The composed gas harm eliminating device 3b has an outer wall 111 of a 4-layered structure similar to that of thermally decomposing device 3a, including an innermost refractory concrete layer 113a, an inner iron plate 112a, an outer refractory concrete layer 113b and an outermost iron plate 112b coated with a heat resisting coating. A portion of the innermost refractory concrete layer 113a positioned under a plurality of second balls (to be described later) 140 is replaced with a heat-resisting refractory firebrick layer (not shown) whose joints are filled with a monolithic refractory such as refractory concrete (not shown) to improve the airtightness of the decomposed gas heating chamber 110.

**[0101]** The heating chamber 110 is heated to a high temperature of about 3000 °C as will be described later. A

temperature at a position distant scores of centimeters from the plurality of second balls 140 is not higher than 200 °C and that the heating chamber 110 is in an oxygenless or vacuum state, so that heat conduction is hardly performed, and therefore, such simple structure will suffice for the outer wall 111.

[0102] The heating chamber 110 for the decomposed gases comprises an airtight rectangular parallelepiped space surrounded by the innermost refractory concrete layer 113a. The innermost refractory concrete layer 113a has two groups of through holes 115 each at its portion corresponding to a respective one of the inlet and outlet ports 120 and 121 for allowing the decomposed and harmless gases to flow therethrough into and out of the heating chamber 110.

[0103] In such arrangement, the decomposed gases introduced from the inlet port 120 are heated and decomposed within the heating chamber 110 to become harmless gases, which are then discharged from the outlet port 121 to the outside.

[0104] The decomposed gas heating chamber 110 is separated by a plurality of (6 in FIG. 10) spaced partitions 116 of a refractory firebrick into a plurality of (7 in FIG. 10) subchambers 110a-110g arranged longitudinally within the device 3b. The foremost subchamber 110a fluid communicates with the inlet port 120 whereas the rearmost subchamber 110g fluid communicates with the outlet port 121.

[0105] Each partition 116 has a plurality of through holes 117 provided at equal intervals through its length so as to cause adjacent subchambers to fluid communicate. In such arrangement, the decomposed gas heating chamber 110 has therein a plurality of straight gas fluid paths extending through the foremost subchamber 110a, through holes 117, subchamber 110b, through holes 117, subchamber 110c, through holes 117, subchamber 110d, through holes 117, subchamber 110e, through holes 117, subchamber 110f, through holes 117 and the rearmost subchamber 110g such that the decomposed gases entering the inlet port 120 flows through them and discharges from the outlet port 121 to the outside.

[0106] A pair of second electrodes consisting of two plate-like carbon electrodes 130 may be each disposed on a respective one of right and left sides of any of the subchambers (the second and fifth subchambers 110b and 110e from the front in FIG. 10) except for the rearmost subchamber 110g. Each carbon electrode 130 has a carbon rod 131 which extends outward through the outer wall 111 of the decomposed gas harm eliminating device 3b.

[0107] The rearmost subchamber 110g is filled with a fiber-like active carbon filter 150 and Bincho charcoal 158 to adsorb hydrocarbon and metals. Each subchamber for which a corresponding pair of carbon electrodes 130 are disposed is filled with a plurality of second balls 140 which have the same composition as the plurality of balls 40 of the first embodiment. A second light emitting heater consists of the plurality of second balls. The filter 150 may be replaced with a particulate active carbon filter. A filter of a material other than carbon may be used if it has sufficient absorptivity.

[0108] The sizes and shapes of the through holes 115 and 117 are not especially limited if the second balls 140 do not pass through the holes. If the second balls 140 each take the form of a sphere, the shape of the through holes 115 and 117 each take the form of a triangle preferably. The through holes 115 and 117 each may take the form of a horizontal or vertical slit. For example, instead of using partitions 116 with through holes 117, a plurality of ceramic pillars may be arranged in parallel to form a plurality of spaced slit-like holes 117, which serve to increase the areas of openings of the through holes 117. Thus, use of the plurality of slit-like holes 115, 117 is preferable when a large amount of decomposed gas flows through the plurality of slit-like holes.

[0109] An opening 152 is provided for each of a pair of carbon electrodes 130 in the decomposed gas harm eliminating device 3b for inspection and maintenance of the inside of the device 3b (inspection of a degree of deterioration and replacement of the plurality of second balls 140 and the carbon electrode 130 concerned).

[0110] Each ceramic cover 153 is fixed with bolts 154 to the outer wall 111 through a refractory sheet (or seal) (not shown) so as to cover a corresponding opening 152 to thereby maintain sufficiently the inner airtightness of the decomposed gas harm eliminating device 3b. Since each refractory concrete block 155 is fitted between the corresponding carbon electrode 130 and ceramic cover 153, the temperature maintenance within the decomposed gas harm eliminating device 3b is sufficiently achieved. Each ceramic cover 153 may be replaced with an iron cover coated with an insulating material. The refractory concrete block 155 may be replaced with a refractory firebrick block.

[0111] Each ceramic cover 153, a corresponding refractory concrete block 155, a corresponding carbon electrode 130, and a corresponding carbon rod 131 compose a united electrode unit 157. Thus, only by replacing an old or defective electrode unit 157 with a new one without replacing the ceramic cover 153, refractory concrete block 155, carbon electrode 130 and carbon rod 131 separately, the old or defective carbon electrode 130 is replaced with a new one easily.

[0112] A rectangular iron frame 156 is provided so as to cover the inner periphery of an outer axial end portion of the corresponding opening 152 provided in the outermost refractory concrete layer 113b. A rectangular iron frame 159 is wound around on an outer axial end portion of the refractory concrete block 155 and also fits in the rectangular iron frame 156 such that the corresponding electrode unit 157 with the rectangular iron frame 159 is slidably moved into/out of the opening 152.

[0113] The decomposed gas harm eliminating device 3b has a plurality of inspection openings 160 provided above subchambers 110b, 110e and 110g in FIGS. 9 and 10 and open in the upper surface thereof such that degrees of

deteriorations in the second balls 140 and the refractory concrete block are inspected and/or, if necessary, the second balls 140 are replaced with another plurality of ones through the respective inspection openings.

[0114] The form of the decomposed gas flow paths is freely designable, for example, so as to be straight or zigzag, depending on the kinds and concentration of harmful substances contained in the decomposed gases and the quantities of the wastes to be decomposed. The number of subchambers filled with the second balls 140, and the quantity of second balls 140 may be adjusted appropriately. While in the present embodiment the decomposed gas flow paths are illustrated as extending horizontally, they may extend vertically.

[0115] A plurality of decomposed gas harm eliminating devices 3b may be attached to the thermal decomposition apparatus 3a depending on the quantities of wastes to be decomposed and the quantities of decomposed gases to be produced. Thus, this applies to facilities which treat of a large amount of wastes.

[0116] A method of thermally decomposing wastes, using the thermal decomposition apparatus 3, will be described next. The door 22 of the thermal decomposition device 3a of the thermal decomposition apparatus 3 is opened, and the wastes are then input into the heating chamber 10 so as to be placed over the plurality of balls 40. The vacuum pump 151 is then activated to evacuate the heating chamber 10 of the thermal decomposition device 3a and the decomposed gas heating chamber 110 of the decomposed gas harm eliminating device 3b to bring about a vacuum state (for example, of either a high vacuum of about  $6.7 \times 10^{-2}$  Pa or a lower vacuum of about 0.02-0.06 MPa). Thus, the plurality of balls 40 within the heating chamber 10 and the plurality of second balls 140 within the decomposed gas heating chamber 110 are also placed in the vacuum state.

[0117] A required voltage is then applied across each pair of carbon electrodes 30 and each pair of carbon electrodes 130 to cause electric discharges between the plurality of balls 40 and between the plurality of second balls 140, respectively. The plurality of pairs of carbon electrodes are connected in series with a power supply (not shown). Although they may be connected in parallel with the power supply, the series connection of the plurality of pairs of carbon electrodes desirably brings about a higher discharge efficiency and a higher temperature.

[0118] Since the discharge regions are at a high temperature of about 3000 °C, the wastes are thermally decomposed into gases as in the first embodiment. The decomposed gases are discharged from the outlet port 21 and fed through the connecting pipe 101 from the inlet port 120 into the decomposed gas heating chamber 110 of the decomposed gas harm eliminating device 3b.

[0119] The introduced decomposed gases come into contact with the electric discharges (sparks) occurring between the plurality of second balls 140 to be heated to a high temperature of about 3000 °C. Thus, when hydrocarbon compounds, carbon dioxide and harmful substances such as dioxin are contained in the decomposed gases, they are thermally decomposed into harmless gases, which may contain remaining hydrocarbon compounds and/or the harmful substances or metals. However, these substances are adsorbed by the filter 150 or Bincho charcoal filter 158 and hardly discharged out of the thermal decomposition apparatus 3 to the outside.

[0120] The decomposed gas harm eliminating device 3b may comprise at least one of (a) a second vacuum meter (not shown) for measuring the pressure within the decomposed gas heating chamber 110 and second pressure adjusting means (not shown) for adjusting to a predetermined value the pressure within the decomposed gas heating chamber 110 based on a measured value of the second vacuum meter; (b) second intervening spacer which contain carbon as a main ingredient (not shown) provided between the plurality of second balls 140 and at least portions of the inner wall of the decomposed gas heating chamber 110 with which the plurality of second balls 140 would otherwise contact; (c) portions of the inner wall of the decomposed gas heating chamber 110 with which the plurality of second balls 140 contact, and being composed of a monolithic refractory containing at least one selected from the group of boron nitride, niobium, silicon carbide, boron carbide, magnesium oxide, hafnium oxide, hafnium dioxide, and beryllium aluminum oxide; and (d) pairs of second electrodes at least part of which takes the form of a rod or horn (not shown) surrounded by the plurality of second balls 140.

(Fourth Embodiment)

[0121] FIG. 11 is a vertical cross-sectional view of a thermal decomposition apparatus 4 for wastes as a fourth embodiment as viewed from its front. FIG. 12 is a horizontal cross-sectional view taken along a line D-D of FIG. 11. The same reference numeral is used to denote identical or similar elements of the thermal decomposition apparatus 4, 1 and 3 of the first, third and fourth embodiments.

[0122] The thermal decomposition apparatus 4 of the fourth embodiment comprises the thermal decomposition device 3a and the decomposed gas harm eliminating device 3b of the third embodiment combined as a unit and is similar in composition to the thermal decomposition apparatus 1 of the first embodiment except that the thermal decomposition apparatus 4 takes the form of a rectangular parallelepiped (the thermal decomposition apparatus 1 of the first embodiment takes the form of two piled rectangular parallelepipeds) and that the heating chamber 10 has a different internal composition. Thus, further description of the identical composition will be omitted and only their different structural portions will be described next.

[0123] Provided on top of the heating chamber 10 is a decomposed gas heating chamber 110 partitioned by horizontal and vertical partitions 16 and 18 of a heat-resisting firebrick. The vertical partition 18 has a plurality of through holes 118 as inlet ports for the decomposed gas. A portion of the innermost refractory concrete layer 13a facing the outlet port 21 has a plurality of through holes 115 which places in fluid communication the heating chamber 110 and the outlet port 21 also functioning as an outlet port for harmless gases.

[0124] In such arrangement, the decomposed gases produced from the wastes by thermal decomposition are introduced from the heating chamber 10 through the through holes 118 into the heating chamber 110, and then through the through holes 115 from the outlet port 21 to the outside of the thermal decomposition apparatus 4.

[0125] The sizes and shapes of the through holes 115 and 118 are not especially limited if the plurality of second balls 140 do not pass through those holes. If the second balls 140 each take the form of a sphere, the shape of the through holes 115 and 118 each take the form of a triangle preferably. The through holes 115 and 118 each may take the form of a horizontal or vertical slit. For example, instead of using partitions 18 with through holes 118, a plurality of ceramic pillars may be arranged in parallel to form a plurality of spaced slit-like holes 118, which serve to increase the opening areas of the through holes 115 and 118. Thus, use of the plurality of slit-like holes 115 and 118 is preferable when a large amount of decomposed gas flows through the holes.

[0126] The heating chamber 110 is filled with the plurality of second balls 140 each in the form of a sphere. Thus, they are in point contact one with another. A second light emitting heater consists of the plurality of second balls 140.

[0127] A pair of second electrodes consisting of two plate-like carbon electrodes 130 are each disposed on a respective one of both ends of the decomposed gas heating chamber 110 (provided in an upper portion of the heating chamber 10) filled with the second balls 140. Each carbon electrode 130 has a carbon rod 131 attached thereto extending axially outward through the corresponding outer wall 11 of the decomposition apparatus 4. The carbon rod 131 may be replaced with a heat-resisting refractory stainless steel rod. It is to be noted that if a stainless steel rod extends through the corresponding carbon electrode 130 so as to be in contact with the second balls 140, the portion of the stainless steel rod in contact with the second balls 140 should be covered with a carbon material so as to prevent its deterioration.

[0128] An opening 152, similar to the opening 52 provided for each of the pair of carbon electrodes 30 is provided for each of a pair of carbon electrodes 130 in the decomposition apparatus 4 for inspection and maintenance of the inside of the heating chamber 110 (inspection of degrees of deteriorations in, and replacement of, the second balls 140 and the carbon electrode 130 concerned).

[0129] Each ceramic cover 153 is fixed with bolts 154 to the outer wall 11 through a refractory sheet (or seal) (not shown) so as to cover a corresponding opening 152 to thereby maintain sufficiently the inner airtightness of the decomposition apparatus 4. Since each refractory concrete block 155 is fitted between the corresponding carbon electrode 130 and the ceramic cover 153, the temperature maintenance within the decomposition apparatus 4 is sufficiently achieved. Each ceramic cover 153 may be replaced with an iron cover coated with an insulating material. The refractory concrete block 155 may be replaced with a refractory firebrick block.

[0130] Each ceramic cover 153, a corresponding refractory concrete block 155, a corresponding carbon electrode 130, and a corresponding carbon rod 131 compose a united electrode unit 157. Thus, only by replacing an old or defective electrode unit 157 with a new one without replacing the ceramic cover 153, refractory concrete block 155, carbon electrode 130 and carbon rod 131 separately, the old or defective carbon electrode 130 is replaced with a new one easily.

[0131] A rectangular iron frame 156 is provided so as to fit fixedly into an edge of the corresponding opening 152 at its edge to thereby cover a corresponding portion of the refractory concrete layer 13b. A rectangular iron frame 159 fits fixedly over an outer axial end portion of the refractory concrete block 155 and also fits in the rectangular iron frame 156 such that the corresponding electrode unit 157 with the rectangular iron frame 159 is slidably moved into/out of the opening 152.

[0132] The decomposition apparatus 4 has an inspection opening 160 provided above the heating chamber 110 and open in the upper surface thereof such that degrees of deteriorations in the second balls 140 and the refractory concrete block are inspected and/or that, if necessary, the second balls 140 are replaced with another plurality of ones through the respective inspection openings.

[0133] The composition of the heating chamber 110 and the quantity of the second balls 140 may be adjusted depending on the kinds and concentrations of harmful substances contained in the decomposed gases and the quantity of wastes to be decomposed.

[0134] A portion of the thermal decomposition apparatus 4 corresponding to the decomposed gas harm eliminating device 3b may comprise at least one of the same elements (a)-(d) as were described above with respect to the decomposed gas harm eliminating device 3b of the third embodiment.

[0135] A method of thermally decomposing the wastes, using the thermal decomposition apparatus 4, will be described next. The door 22 of the thermal decomposition apparatus 4 is opened, and the wastes are then cast into the heating chamber 10 so as to placed over the plurality of balls 40. The vacuum pump 51 is then activated to evacuate

the thermal decomposition apparatus 4 to bring about a vacuum state (for example, of either a high vacuum of about  $6.7 \times 10^{-2}$  Pa or a lower vacuum of about 0.02-0.06 MPa). Thus, the plurality of balls 40 within the heating chamber 10 and the plurality of second balls 140 within the decomposed gas heating chamber 110 are also placed in the vacuum state.

[0136] A required voltage is applied across each of the first and second pairs of carbon electrodes 30 and 130 to cause electric discharges between the plurality of first balls 40 and between the plurality of second balls 140. Since the respective discharge regions are at a high temperature of about 3000 °C and hence the wastes are thermally decomposed into gases as in the first embodiment and introduced through the respective groups of through holes 118 into the decomposed gas heating chamber 110. Since the discharge regions occurring between the plurality of second balls 140 are also at a high temperature of about 3000 °C, the decomposed gases in contact with the discharge regions are also heated to about 3000 °C. Thus, even when hydrocarbon compounds, carbon dioxide, and harmful substances such as dioxin remain in the decomposed gases, they are thermally decomposed into harmless gases. Furthermore, the harmless gases pass through the through holes 115 and the filter 50. Thus, even when hydrocarbon compounds and harmful substances still remain in the harmless gases, or even when the harmless gas contains metals, they are adsorbed by the filter 50 without being almost discharged out of the thermal decomposition apparatus 4, and only harmless low molecular-weight substances are discharged out of the apparatus 4.

[0137] A small compact thermal decomposition apparatus for wastes in which the thermal decomposing device and the decomposed gas harm eliminating device are combined as a unit is greatly suitable for use in small-scaled facilities which discharge a small amount of general wastes.

#### (Fifth Embodiment)

[0138] FIG. 13 is a vertical cross-sectional view of a thermal decomposition apparatus 5 for wastes as a fifth embodiment as viewed from its side. The same reference numeral is used to denote identical or similar elements of the thermal decomposition apparatus 5, 1, 3 and 4 of the first, third and fourth embodiments.

[0139] The thermal decomposition apparatus 5 of the fifth embodiment comprises the thermal decomposition device 3a and the decomposed gas harm eliminating device 3b of the third embodiment combined as a unit as in the fourth embodiment and is similar in composition to the thermal decomposition apparatus 4 of the fourth embodiment except that the thermal decomposition apparatus 5 is of a larger-scaled type and that the heating chamber 10 has a different internal composition. Thus, further description of the identical composition will be omitted and only their different structural portions will be described next.

[0140] Provided on top of the heating chamber 10 is a decomposed gas heating chamber 110 partitioned by horizontal and vertical partitions 16 and 18 of a heat-resisting firebrick as in the decomposition apparatus 4 of the fourth embodiment. The vertical partition 18 has a plurality of through holes 118 as inlet ports for the decomposed gas. A portion of the innermost refractory concrete layer 13a facing the outlet port 21 has a plurality of through holes 115 which place in fluid communication the heating chamber 110 and the outlet port 21 also functioning as an outlet port for harmless gases.

[0141] The decomposed gas heating chamber 110 is separated by a plurality of (2 in FIG. 13) spaced partitions 116 of a refractory firebrick into a plurality of (3 in FIG. 13) subchambers 110a, 110b, 110c arranged longitudinally (right and left in FIG. 13) within the apparatus 5. The foremost subchamber 110a (the left one in FIG. 13) fluid communicates through holes 118 with the heating chamber 10 whereas the rearmost subchamber 110c fluid communicates through holes 115 with the outlet port 21. Each partition 116 has a plurality of through holes 117 provided at equal intervals through its length so as to place adjacent subchambers in fluid communication.

[0142] In such arrangement, the thermally decomposed gases produced from the wastes are introduced from the heating chamber 10 through the through holes 118 into the decomposed gas heating chamber 110, and thence pass through the subchamber 110a, through holes 117, subchamber 110b, through holes 117, subchamber 110c, through holes 115, and then discharge from the outlet port 21 to the outside.

[0143] The subchambers (110a, 110b in FIG. 13) other than the rearmost subchamber 110c are filled with a plurality of second balls 140 each in the form of a sphere, which balls are in point contact one with another. A second light emitting heater consists of the plurality of second balls 140.

[0144] The rearmost subchamber 110c is filled with a fiber-like active carbon filter 50. It is to be noted that no active carbon filter is provided within the exhaust pipe 23. The filter 50 may be replaced with a particulate active carbon filter. A filter of a material other than carbon may be used if it has sufficient absorptivity.

[0145] The sizes and shapes of the through holes 115, 117 and 118 are not especially limited if the second balls 140 do not pass through those holes. If the second balls 140 each take the form of a sphere, the shape of the through holes 115, 117 and 118 each take the form of a triangle preferably. The through holes 115, 117 and 118 each may take the form of a horizontal or vertical slit. For example, instead of using the partitions 116 with through holes 117, a plurality of ceramic pillars may be arranged in parallel to form a plurality of spaced slit-like holes 117, which serve to increase

the opening areas of the through holes 115, 117 and 118. Thus, use of the plurality of slit-like holes is preferable when a large amount of decomposed gas flows through them.

[0146] A pair of second electrodes consisting of two plate-like carbon electrodes (which are not shown in FIG. 13, but which have a similar composition to the pair of carbon electrodes 130 in the fourth embodiment) are each disposed on a respective one of both sides of each subchamber filled with the second balls 140. Each carbon electrode has a carbon rod (which is not shown in FIG. 13, but which has a similar composition to the carbon rod 131 in the fourth embodiment) attached thereto and extending axially outward through the corresponding outer wall 11 of the decomposition apparatus 5.

[0147] In the thermal decomposition apparatus 5 (not shown in FIG. 13), the compositions of the carbon electrodes and rods, electrode units and openings are similar to those of the electrode units 157 and openings 152 of the thermal decomposition apparatus 4 of the fourth embodiment, and further description thereof will be omitted.

[0148] The decomposition apparatus 5 has three inspection openings 160 each provided above a respective one of the subchambers 110a, 110b and 110c and open in the upper surface thereof such that degrees of deteriorations in the second balls 140 and the refractory concrete blocks are inspected and/or that, if necessary, the second balls 140 are replaced with another plurality of ones through the respective inspection openings.

[0149] In the decomposition apparatus 5, the size of the heating chamber 10 may be adjusted depending on the kinds and quantity of the wastes to be decomposed. Furthermore, the number of subchambers each filled with the second balls 140 and the quantity of second balls 140 may be adjusted appropriately depending on the kinds and concentrations of the harmful substances contained in the decomposed gases.

[0150] A portion of the thermal decomposition apparatus 5 corresponding to the decomposed gas harm eliminating device 3b may comprise at least one of the same elements (a)-(d) as were described above with respect to the decomposed gas harm eliminating device 3b of the third embodiment.

[0151] A method of thermally decomposing the wastes, using the thermal decomposition apparatus 5, will be described next. The door 22 of the thermal decomposition apparatus 5 is opened, and the wastes are then cast into the heating chamber 10 so as to be placed over the plurality of balls 40. The vacuum pump 51 is then activated to evacuate the thermal decomposition apparatus 5 to bring about a vacuum state (for example, of either a high vacuum of about  $6.7 \times 10^{-2}$  Pa or a lower vacuum of about 0.02-0.06 MPa). Thus, the plurality of balls 40 within the heating chamber 10 and the plurality of second balls 140 within the decomposed gas heating chamber 110 are also placed in the vacuum state.

[0152] A required voltage is applied across each of the first and second pairs of carbon electrodes (none of them are shown in FIG. 13) within the heating chambers 10 and 110 to cause electric discharges between the first plurality of balls 40 and between the second balls 140. Since the respective discharge regions are at a high temperature of about 3000 °C and hence the wastes are thermally decomposed into gases as in the first embodiment and introduced through the respective groups of through holes 118 into the decomposed gas heating chamber 110. Since the discharge regions occurring between the second balls 140 are also at a high temperature of about 3000 °C, the decomposed gases in contact with the discharge regions are also heated to about 3000 °C while the decomposed gases are passing through the subchambers (110a, 110b in FIG. 13). Thus, even when hydrocarbon compounds, carbon dioxide, and harmful substances such as dioxin remain in the decomposed gases, they are thermally decomposed into harmless gases.

[0153] Furthermore, the harmless gases pass through the filter 50. Thus, even when hydrocarbon compounds, harmful substances and metals still remain in the harmless gases, they are adsorbed by the filter 50 without being almost discharged out of the thermal decomposition apparatus 5, and only harmless low molecular-weight substances are discharged out of the apparatus 5.

[0154] The large-scaled thermal decomposition apparatus 5 which comprises the thermal decomposition device and the decomposed gas harm eliminating device united as a unit thermally decomposes a large amount of waste compared to the thermal decomposition apparatus 4 of the fourth embodiment. Thus, the thermal decomposition apparatus 5 is greatly suitable for use in facilities (an eating house or restaurant, hospital or factory) which produce a large amount of waste compared to general households.

[0155] The thermal decomposition apparatus 5 may be further increased in size. In this case, it is capable of disposing of a large amount of wastes, so that it is suitable for use in facilities (for example, a large-scaled factory) which discharge a large amount of wastes.

(Sixth Embodiment)

[0156] In the thermal decomposition apparatus 1-5 of the first-fifth embodiments, at least portions of the inner walls (made of the refractory concrete layer 13a and the heat-resisting refractory firebrick layer 14) of the heating chamber 10 or at least portions of the inner walls (the refractory concrete layer 113a and heat resisting firebrick (not shown)) of the heating chamber 110 with which the first or second balls 40 or 140 are in contact may each comprise a plurality of convexities to thereby reduce the respective quantities of the first or second balls 40 or 140.

[0157] FIGS. 14 (a) and (b) are a vertical cross-sectional view (corresponding to FIG. 3) and a horizontal cross-sectional view, respectively, of a lower portion of the heating chamber 10 of the thermal decomposition apparatus 1-5 for wastes. The same reference numeral is used to denote the identical or similar elements of the first and sixth embodiments.

[0158] The thermal decomposition apparatus of this embodiment is similarly in composition to that of the first embodiment and further description of the identical or similar structural elements thereof will be omitted and only different structural portions thereof will be described next.

[0159] The heating chamber 10 has on its bottom (made of a heat-resisting refractory firebrick layer 14) a plurality of equally spaced parallel convex spacers of a triangular cross-section 15 extending by a length equal to a related pair of electrodes 30 perpendicular to the surfaces of the pair of carbon electrodes 30.

[0160] A plurality of balls 40 are disposed in groups between the respective parallel spacers 15. The number of balls 40 is reduced due to fact that the plurality of balls 40 are divided by the spacers 15 into a plurality of groups, and the use of the inclined surfaces 15a of the spacers 15. Thus, a quantity of electric power to be used is reduced, economically.

[0161] The spacers 15 may have the same quality as the inner wall of the heating chamber 10 (refractory concrete or heat-resisting refractory firebrick) or carbon such as high-density impermeability carbon or graphite. If the spacers 15 produce effects such as were mentioned above, the shape of the spacers 15 is not limited to a triangle in cross section.

(Seventh Embodiment)

[0162] A thermal decomposition apparatus 7 of this embodiment comprises a group of intervening pillar-like impermeability carbon spacers 19 of a semicircular cross section provided, respectively, between the inner wall (of the refractory concrete layer 13a and heat-resisting refractory firebrick layer 14) of the heating chamber 10 and the plurality of balls 40 or between the inner wall (of the refractory concrete layer 113a and heat-resisting refractory firebrick layer (not shown)) of the heating chamber 110 and the plurality of second balls 140 in the relevant thermal decomposition apparatus 1-5 of the first-fifth embodiments. Thus, the plurality of balls 40 or 140 are not in contact with the inner wall of the heating chamber 10 or 110, so that the probability that the inner walls of the heating chambers will be deteriorated or melted due to high temperature produced from the plurality of balls 40 or 140 is reduced.

[0163] The intervening spacers 19 each may take the form of a pipe of a semicircular cross section or the form of a plate so as to cover a portion of the inner wall of the heating chambers with which the plurality of balls 40 or 140 would otherwise contact.

[0164] FIG. 15 is a vertical cross-sectional view of the thermal decomposition apparatus 7. The same reference numeral is used to denote the identical or similar elements of the thermal decomposition apparatus of the first and seventh embodiments.

[0165] The thermal decomposition apparatus 7 of the present embodiment is similar in composition to that of the first embodiment, and further description of the same similar structural portions thereof will be omitted and only different structural portions thereof will be explained next.

[0166] A plurality of intervening spacers 19 having a semicircular cross section are provided at predetermined intervals parallel to, and between, the surfaces of a pair of plate-like carbon electrodes 30 on the bottom (of a heat-resisting refractory firebrick 14) of the heating chamber 10. A second plurality of intervening spacers 19 having the same cross section are disposed perpendicular to the bottom of the heating chamber 10 along its lower inner portion (with which the plurality of balls 40 would otherwise contact) at the predetermined intervals between the pair of carbon electrodes 30 such that their flat surfaces are in contact with the inner wall or bottom of the heating chamber 10 with their cylindrical surfaces facing the heating chamber 10. The interval between any adjacent intervening spacers 19 is smaller than the diameter of one of the balls 40 used.

[0167] The spacers 19 are each made of high-density impermeability carbon and graphite.

[0168] The spacers 19 may be disposed perpendicular to the surfaces of the pair of plate-like carbon electrodes 30.

[0169] The spacers 19 may include pillars of a circular cross section buried partly in the inner wall and bottom of the heating chamber 10 such that they protrude in 1/2-2/3 of their diameter into the heating chamber 10.

[0170] As described above, the plurality of intervening spacers of a semicircular cross section 19 are provided between the inner wall of the heating chamber 10 and the plurality of balls 40 to separate the inner wall and bottom of the heating chamber 10 from the plurality of balls 40. Thus, there is substantially no probability that the inner wall and bottom of the heating chamber 10 will be deteriorated and/or melted by heat.

[0171] Since the intervening spacers 19 each have a circular surface, they are in point contact with the plurality of balls 40. Thus, no general electrically conductive state occurs, but electric discharges with high efficiency are achieved.

[0172] In addition, since the intervening spacers 19 in contact with the plurality of balls 40 are each made of high-density impermeability carbon and graphite, so that even when the light emitting heater 41 are heated to about 5000 °C beyond 3000 °C, they withstand that temperature.

[0173] The spacers 19 may be made of refractory concrete or heat-resisting refractory firebrick as in the material of the inner wall of the heating chamber 10. In that case, however, it has only heat resistance up to about 3000 °C.

[0174] In the present embodiment a voltage applied first is 400-500 V to thereby feed high power to the light emitting heater 41 to thereby increase their temperature to 5000 °C rapidly, at which temperature almost all materials and gases are decomposed including even ashes which includes leavings in general incinerators to leave nothing. Since the decomposing speed is high, a large amount of wastes continue to be decomposed constantly. Once the heating chamber reaches 5000 °C, about 30 V will suffice for the voltage applied across the pairs of carbon electrodes and hence the decomposition apparatus 7 is operated at low cost.

[0175] Even when the light emitting heater 41 are heated to a high temperature of about 5000 °C, the heating chamber 10 is in an oxygenless or vacuum state. Thus, a position distant from about 20-30 cm from the light emitting heater 41 is at a very low temperature and hence there is no need for cooling the thermal decomposition apparatus 7.

[0176] The invention effectively uses the physical property of superconductivity that carbon and graphite exhibit at ultrahigh temperatures.

[0177] By applying the structures of the inner wall and bottom of such heating chamber 10 to the decomposed gas harm eliminating device 3b, the decomposed gases are made harmless efficiently.

[0178] A thermal decomposition apparatus 7 may be operated in a manner similar to that mentioned above in a state where a light emitting heater unit comprising the plurality of spacers 19 and the plurality of balls 40 as a unit is disposed between the pair of carbon electrodes 30.

[0179] An example of such composition will be described with reference to FIGS. 16 and 17. FIG. 16 is a perspective view of a mount 80 on which the plurality of intervening spacers 19 are to be fixed. FIG. 17 (a) and (b) are a side view and a plan view of the mount 80 on which two groups of spacers 19 are fixed.

[0180] The mount 80 includes a rectangular frame 81 which has downward extending legs 82. Additional legs 82 may be provided at corresponding midpoints of respective sides of the frame 81.

[0181] A plurality of horizontally extending intervening spacers 19 of a circular cross section are fixed at predetermined intervals across a pair of parallel sides of the frame 81. A second pair of upward extending intervening spacers 19 are fixed at their lower ends parallel to each other to the pair of parallel sides of the frame 81. The interval between any adjacent spacers 19 should be smaller than the diameter of each balls 40. Each spacer 19 may have a semi-circular cross section. A plurality of balls 40 are placed on the plurality of horizontally extending spacers 19 fixed on the mount 8 in a space surrounded by the second plurality of spacers 19 to form a united light emitting heater unit comprising the plurality of balls and the first and second plurality of spacers.

[0182] Since the plurality of balls 40 are surrounded by the intervening spacers 19 disposed on the bottom and periphery of the mount 80, the plurality of balls 40 are not in contact with the inner wall and bottom of the heating chamber 10, which therefore are hardly deteriorated and/or melted by the heat produced within the heating chamber 10.

[0183] Since the respective spacers 19 each have a circular cross section, they are in point contact with the balls 40. Thus, no regular electric conduction occurs, but electric discharges with high efficiency occur.

[0184] If the thermal decomposition apparatus 7 further has an opening in its front for moving the light emitting heater unit into and out of the heating chamber in addition to the openings 52 each provided on a respective one of the opposite sides of the decomposition apparatus 7, replacement of the plurality of balls 40 is greatly facilitated, advantageously. In addition, cleaning a small amount of leavings, and repair, inspection and replacement of the light emitting heater unit and the electrode unit 57 can be easily performed in three directions, advantageously.

[0185] The intervening spacers 19 are each made of high-density impermeability carbon and graphite. The material of the mount 80 is not limited as long as it has sufficient heat resistance. A simple iron plate will suffice for the mount 80 and hence repair, inspection and/or replacement of the light emitting heater unit is easily performed.

(Eighth Embodiment)

[0186] A thermal decomposition apparatus of this embodiment comprises a combination of each of the thermal decomposition apparatus 1-5 and 7 of the first-seventh embodiments with a plurality of pairs of horn-like or sharp-tipped rod electrodes 30a/130a each pair of horn electrodes 30a/130a being provided on a respective one of the corresponding pair of plate-like carbon electrodes 30/130 so as to extend axially inward perpendicular to the corresponding surface of the carbon electrode 30/130. FIG. 18 is a perspective view of a pair of horn electrodes 30a attached to a carbon electrode 30.

[0187] In such arrangement, the number of points where the first/second plurality of balls 40/140 are in contact with the corresponding electrodes 30/130 increases to thereby increase the discharge efficiency and hence to obtain a high temperature of about 3000 °C in a shorter time than the other embodiments.

[0188] The horn-like or sharp-tipped electrodes 30a/130a may be replaced with corresponding polygonal pillar-electrodes although the latter is somewhat inferior in point contact compared to the former. The electrodes 30a/130a are not necessarily required to have a sharp tip or may take the form of a rod. Although a pair of horn electrodes 30a/130a



are preferably attached perpendicular to the corresponding surface of a plate-like carbon electrode, they are not necessarily required to be so. The number of horn electrodes 30a/130a to be attached to one plate electrode is not limited, but usually about 1-5. The horn electrodes 30a/130a are usually the same in material as the carbon electrodes 30/130.

5 (Ninth Embodiment)

[0189] A thermal decompositions apparatus of this embodiment comprises an improvement to the thermal decomposition apparatus 1-5 and 7 of the first-eighth embodiments which in turn comprises at least portions of the inner walls (refractory concrete layer 13a and heat-resisting firebrick 14) of the heating chamber or at least portions of inner walls  
10 (refractory concrete layer 113a and heat-resisting firebrick (not shown)) of the heating chamber 110 with which the plurality of balls 40 or 140 contact are composed of a monolithic refractory (refractory concrete or heat-resisting firebrick) containing boron nitride.

[0190] Boron nitride has a melting point of 3000 °C and has an electric insulation at high temperatures. Thus, the portions of the inner walls of the heating chamber 10 or 110 with which the plurality of balls 40 or 140 contact have  
15 improved heat resistance such that they are hardly deteriorated/melted even at a high temperature of about 3000 °C.

[0191] Instead of the monolithic refractory containing boron nitride, a monolithic refractory containing at least one selected from the group of boron nitride, niobium, silicon carbide, boron carbide, magnesium oxide, hafnium oxide, hafnium dioxide, and beryllium aluminum oxide.

[0192] A method of making, and a physical property of, first and second pluralities of balls 40 and 140 each made  
20 of graphite, used in the above respective embodiments, will be described next in detail.

(Example 1)

[0193] Fifty five weight parts of phenol resin was mixed with 45 weight parts of acrylic fiber having a length of 0.1-0.5  
25 mm. Instead of the phenol resin, a polydivinyl benzene resin may be used. Instead of acrylic fiber, animal/plant fibers or a mixture of acrylic fibers and animal/plant fibers may be used. Those fibers such as the acrylic fibers were carbonized in the process of making the balls for the light emitting heater to become carbon fibers within the balls.

[0194] The above mixture of phenol resin and acrylic fiber was filled into a mold, and then heated and pressed sufficiently to cure the phenol resin to form spheres (for example, of a diameter of 33 mm). The molding may take the  
30 form of a hemisphere, rectangular parallelepiped or pillar. In the case of hemisphere, two hemispheres were joined to form a sphere in this stage. Those moldings may have holes or concavities into which desired ingredients are to be injected.

[0195] The moldings were then subjected to a flame resistance process at 250-300 °C, and then carbonized at 1000-1500 °C under an inert gas. The obtained carbon was then graphitized at 2000-3000 °C to, and the graphite was  
35 then subjected to a sizing process (surface processing).

[0196] In the carbonization and graphitization, the half-finished product graphite was burnt repeatedly in an inert gas under an isotropic pressure of not less than 30 MPa in hot isostatic pressing (HIP) to increase the density of the graphite. The HIP is also a method capable of applying isotropic pressure to a sphere.

[0197] General graphite or carbon has in its surface and inside many pores, whose total surface is generally about  
40 25 % of the whole surface area thereof. By the above-mentioned process, the total area of the pores in the surface and inside of the graphite was reduced to 10 % or less of the whole surface area of the graphite and according to circumstances, to 5 % or less.

[0198] By using a phenol resin as a filler, graphite having a relatively small number of pores was obtained. By further burning this graphite under pressure as described above, impermeability graphite of a higher accuracy was obtained.  
45 Such impermeability graphite had corrosion resistance to almost all chemicals in a wide practical range of temperatures. It also had very high heat conductivity compared to general corrosion resistance materials. It also had a high thermal stability which was hardly affected adversely by rapid changes in the temperature thereof.

[0199] The quantity of the phenol resin to be added is preferably in a range of 10-60 weight parts. When the quantity of the phenol resin exceeds 60 weight parts, the specific gravity of the resulting impermeability graphite is reduced and bubbles are liable to be produced within the graphite and/or unhardened portions (gel-like portions) are liable to remain within the graphite. In addition, in the carbonization and graphitization, pressure is difficult to apply isotropically to the graphite. If the quantity of the phenol resin is less than 10 weight parts, it is difficult to mold a mixture of the phenol resin and acrylic fibers as a unit. In order to secularly prevent the occurrence of such problems, the quantity of the phenol resin to be added is preferably 20-55 weight parts. It is to be noted that when the thermal shock resistance  
55 is considered, the quantity of the phenol resin is only required to be sufficient to harden the acrylic fibers and should be preferably reduced.

[0200] By such processing, the balls for light emitting heater each in the form of a sphere having a diameter of 30 mm are obtained. When the half-finished products each take the form of a rectangular parallelepiped or pillar, they are

each ground to balls taking the forms of a sphere.

[0201] Since these balls are each made of impermeability graphite, they have absorptivity of not higher than that of rubber, a strength of two-three times that of general graphite, a hardness of not less than 65 (in Example 1, 68), a density of not less than 1.87 g/cm<sup>3</sup> (adjustable depending on a ratio in mixture of fibers), a tensile strength of 16.7 MPa, a bending strength of 35.3 MPa, a compression strength of 98.0 MPa, a modulus of elasticity of not less than 12700 MPa, a coefficient of thermal expansion of  $3.0 \times 10^{-6}/^{\circ}\text{C}$ , a thermal conductivity of 151 W/m · °C, and a heat resistance of 3000 °C. For chemical property, they exhibit excellent corrosion resistance to chemicals having a strong acidity such as concentrated sulfuric acid and nitric acid, and chemicals having strong alkalinity such as sodium hydroxide. It is to be noted that when graphite is made from a phenol resin, its alkalinity can be reduced somewhat. Results of a corrosion resistance test are shown in Tables 1-3. The term "all" used in a concentration item of each of Tables 1, 2 and 3 represents "all concentrations".

[0202] Since these balls for light emitting heater are made of impermeability graphite, as described above, they have the following excellent characteristics:

- (1) they are hardly to be deteriorated by the chemicals contained in the harmful substances mentioned above;
- (2) they are difficult to react with oxygen in the atmosphere and oxygen produced by decomposition of the wastes. Thus, they are difficult to deteriorate and produce few carbon monoxide and/or carbon dioxide;
- (3) they have a high strength, so that they are hardly ground to thereby have an high durability;
- (4) they have only a small number of pores, and hence are difficult to adsorb harmful substances mentioned above. They adsorb few gas and hence hardly releases the adsorbed gas at high temperature, if any;
- (5) they exhibit excellent electric and thermal conductivities; and
- (6) they have high resistance to shocks due to rapid changes in the temperature thereof.

[0203] The balls of Example 1 are usable even in the air without any problems. If they are used in a vacuum or oxygenless state, they are difficult to oxidize/deteriorate, so that such state is preferable for use of such balls. Especially, in the vacuum state, the discharge efficiency is high and high temperature is easily obtained with a small amount of power to thereby reduce a cost required for obtaining such high temperature.

(Table 1)

Chemicals' name	Concentration (% by weight)	Temperature (°C)	Corrosion <sup>1)</sup> resistance
[acid]			
hydrochloric acid	All	boiling point	A
nitric acid	10~40	60	B
hydrofluoric acid	48	boiling point	A
hydrofluoric acid	48~60	90	A
sulfuric acid	25~75	130	A
phosphoric acid	85	boiling point	A
phosphoric acid	96	100	A
chromic acid	10	93	B
acetic acid	all	boiling point	A
oxalic acid	all	boiling point	A
sulfurous acid			
(sulfurous acid gas saturated)	-	room temp.	A
hydrochloric acid			
(chlorine gas saturated)	20	boiling point	A
hydrofluoric acid + nitric acid	5/15	93	A

1) A: not at all corroded  
B: hardly corroded

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(Table 2)

5	Chemicals' name	Concentration (% by weight)	Temperature (°C)	Corrosion <sup>1)</sup> Resistance
	[alkali]			
	rayon spinning solution	-	boiling point	A
	caustic soda aqueous solution	67	boiling point	A
	caustic soda aqueous solution	67-80	125	A
	[salt aqueous solution]			
10	zinc chloride	All	boiling point	A
	iron chloride	All	100	A
	sodium chloride	All	boiling point	A
	sodium hypochloride	5	room temp.	A
15	ammonium persulfate	All	18	A
	copper sulfate	All	boiling point	A
	[halogen]			
20	Chlorine	100	170	A
	chlorine water	Saturated	room temp.	A

1) A: not at all corroded  
B: hardly corroded

(Table 3)

25	Chemicals' name	Concentration (% by weight)	Temperature (°C)	Corrosion <sup>1)</sup> Resistance
	[organic compound]			
30	acetone	100	boiling point	A
	ethyl alcohol	95	boiling point	A
	carbon tetrachloride	100	boiling point	A
	ethane tetrachloride	100	boiling point	A
35	chloroform	100	boiling point	A
	kerosine	100	boiling point	A
	Dowtherm <sup>2)</sup>	100	170	A
	benzene	100	boiling point	A
40	benzene (saturated with chlorine)	100	60	A
	benzyl chloride	100	170	A
	methyl alcohol	100	boiling point	A
	monochlorobenzene	100	boiling point	A

1) A: not at all corroded  
B: hardly corroded

2) Heat medium manufactured by the Dow Chemical Co.

## (Example 2)

50 **[0204]** Since a method of making this example is similar to that of Example 1 except for the materials to be used, further description of portions of the present method similar to those of the method used for making Example 1 will be omitted, and only different portions of the present method from those of the method making Example 1 will be described next.

55 **[0205]** The balls for light emitting heater each in the form of a sphere were made in a manner similar to that used for making Example 1 except that graphite powder (99.5 % of fixed carbon having an average grain size of 4 μm) was used instead of the acrylic fibers of Example 1. The graphite powder may be replaced with carbon black powder, coke, charcoal powder such as Japanese Bincho charcoal powder, or a mixture of at least two of those materials.

[0206] The balls for light emitting heater, thus obtained, exhibited excellent characteristics similar to those of the balls for light emitting heater of Example 1.

(Example 3)

[0207] Since a method of making this example is similar to that of Example 1 except for the materials used, further description of portions of the present method similar to those of the method used for making Example 1 will be omitted and only different portions of the present method from those of the method of making Example 1 will be described next.

[0208] Fifty five weight parts of a phenol resin, 40 weight parts of graphite powder (including 99.5 % of fixed carbon having an average grain size of 4  $\mu\text{m}$ ), and 5 weight parts of carbon fibers were mixed. Instead of the phenol resin, a polydivinyl benzene resin may be used. The graphite powder may be replaced with carbon black powder, coke, charcoal powder such as Japanese Bincho charcoal powder, acrylic fibers, animal or plant fibers or a mixture of at least two selected from those ingredients.

[0209] By processing the mixture of the phenol resin, graphite powder and carbon fibers in a manner similar to that used for making Example 1, the balls for light emitting heater of impermeability graphite of high density having a reduced number of pores were each made in the form of a sphere.

[0210] The balls, thus obtained, had excellent characteristics similar to those of the balls of Example 1 as well as an increased strength due to inclusion of the added carbon fibers.

[0211] Preferable quantities of phenol resin, graphite powder and carbon fibers to be added were 10-60, 30-89 and 1-10 weight parts, respectively. The balls for light emitting heater of various characteristics were made in the combination of the respective ranges. When the quantity of the phenol resin exceeds 60 weight parts, troubles such as were described with reference to Example 1 can occur. When the quantity of the phenol resin is less than 10 weight parts, it was difficult to form a molding of phenol resin and graphite powder as a unit. In order to surely preventing the above problems from occurring, the quantity of phenol resin to be added is more preferably 20-25 weight parts. In terms of heat shock resistance, an added quantity of phenol resin required for hardening the graphite powder will suffice for making Example 3. Addition of a less quantity of phenol resin is more preferable.

[0212] When the amount of carbon fiber to be added was less than 1 weight part, the intensity of the resulting balls was not so improved whereas when it exceeded 10 weight parts, cracks were liable to occur in the resulting balls. Three-seven weight parts of carbon fiber to be added are more preferable in terms of a tradeoff between the strength of the resulting balls and the degree of difficulty of crack occurrence.

(Example 4)

[0213] Since a method of making this example is similar to that of Example 1 except for the materials used, further description of portions of the present method similar to those of the method used for making Example 1 will be omitted and only different portions of the present method from those of the method of making Example 1 will be described next.

[0214] Fifty five weight parts of a phenol resin, 40 weight parts of graphite powder (including 99.5 % of fixed carbon having an average grain size of 4  $\mu\text{m}$ ), and 5 weight parts of tungsten powder (having an average grain size of about 1.0  $\mu\text{m}$ , a bulk specific gravity (no load) of 4.22, and a purity of 99.9 % or more) were mixed. Instead of phenol resin, a polydivinyl benzene resin may be used. The graphite powder may be replaced with carbon black powder, coke, charcoal powder such as Japanese Bincho charcoal powder, acrylic fibers, animal or plant fibers or a mixture of at least two selected from those ingredients. The tungsten powder may be replaced with titanium powder (having an average grain size of about 1.0  $\mu\text{m}$ , a bulk specific gravity (no load) of 1.5-2.0, and a purity of 99.9 % or more) or a mixture of tungsten powder and titanium powder.

[0215] By processing the mixture of phenol resin, graphite powder and tungsten powder in a manner similar to that used for making Example 1, balls for light emitting heater of impermeability graphite of high density with a small number of pores were each made in the form of a sphere. Unlike Example 1, the balls of the present Example contained tungsten. In addition, the final step of the graphitization included heat treatment of the half-finished products at about 3000 °C in an inert gas.

[0216] Tungsten was heated at a temperature of about 3000 °C to change to ditungsten carbide ( $\text{W}_2\text{C}$ , a formula weight of 379.71, a density of 17.2 g/cm<sup>3</sup>, a Mohs' hardness of 9, an electric resistibility of 81  $\mu\Omega/\text{cm}$  (25 °C)). Titanium was also heated at a temperature of about 3000 °C to change to titanium carbide ( $\text{TiC}$ , a formula weight of 59.90, a melting point of 3140  $\pm$  90 °C, a boiling point of 4300 °C, a density of 4.94 g/cm<sup>3</sup>, and an electric resistibility of 193  $\mu\Omega/\text{cm}$  (at room temperature)). When  $\text{W}_2\text{C}$  was heated at a temperature of not lower than 2400 °C, its crystal form became a stable  $\beta$  type.

[0217] Titanium has a boiling point of 1675 °C, a boiling point of 3262 °C, and a density of 4.54 g/cm<sup>3</sup>. When it changed to titanium carbide, its melting and boiling points greatly increased and its density increased as well. Tungsten has melting and boiling points of 3387 and 5962 °C, respectively.

[0218] The balls for light emitting heater of impermeability graphite containing at least one of ditungsten carbide and titanium carbide had, in addition to the above-mentioned features (1)-(6) of Example 1, corrosion resistance, mechanical strength (a high hardness, a modulus of elasticity of 310000-440000 MPa) and heat resistance (to 3000 °C or more) excellent compared to the balls of Example 1 which contained none of ditungsten carbide and titanium carbide. In addition, they had a high electric conductivity (electric resistibility of not more than  $70\mu\Omega/\text{cm}$ , (in the present example,  $10\mu\Omega/\text{cm}$ )), and a high electric discharge efficiency.

[0219] The heat treatment of the half-finished products at about 3000 °C in the inert gas produced the following advantage:

- (a) after the heat treatment, the balls for light emitting heater were not required to be subjected to a finishing process or step such as bright heat treatment (of polishing the surfaces of the balls);
- (b) the balls were hardly deformed in use; and
- (c) the heat treatment caused no pollution to the public.

[0220] The quantities of phenol resin, graphite powder and tungsten powder to be added are preferably 10-60, 20-89, 1-20 weight parts, respectively. When the quantity of phenol resin to be added is out of the above range, troubles such as were described in Example 3 would occur. When more than 10 weight parts of the tungsten powder is added, the quantity of phenol resin to be added is preferably 20-60 weight parts in order to mold the mixture of phenol resin, graphite powder and tungsten powder as a unit.

[0221] When the amount of tungsten powder to be added was less than 1 weight part, the mechanical properties, corrosion resistance and heat resistance were not substantially improved. When it exceeded 20 weight parts, the mechanical properties conversely deteriorated to thereby cause cracks in the resulting balls or reduce the processability of the balls. In order to improve the mechanical properties, corrosion resistance and heat resistance sufficiently, and to surely prevent the occurrence of the cracks in the balls and the problem of ball processability, the amount of tungsten powder to be added is preferably 5-10 weight parts.

[0222] The problems of cracks in the balls and of the ball processability are liable to occur when the balls are each made of two hemispheres joined as a unit whereas when they are each molded in the form of a sphere from the beginning, the problems are difficult to occur. Thus, if the balls for light emitting heater each having holes and concavities are molded from their materials and tungsten powder is then injected into the holes and concavities, there is little probability that the above problems will occur even if the quantity of tungsten powder to be added exceeds 10 weight parts. Thus, if the quantity of tungsten powder to be added is between 10 and 20 weight parts, the above-mentioned method is preferably employed.

(Example 5)

[0223] In this Example, a quantity of graphite powder used is larger than that of phenol resin. This Example is exactly the same as Example 1 except for the ingredients to be used. Thus, further description of the identical portions of Examples 1 and 5 will be omitted and only different portions of Example 5 from Example 1 will be described next.

[0224] Twenty weight parts of phenol resin, 70 weight parts of graphite powder (including 99.5 % of fixed carbon having an average grain size of  $4\mu\text{m}$ ), and 10 weight parts of tungsten powder (having an average grain size of about  $1.0\mu\text{m}$ , and a purity of 99.9 % or more) were mixed. Instead of phenol resin, a polydivinyl benzene resin may be used. The graphite powder may be replaced with carbon black powder, coke, charcoal powder such as Japanese Bincho charcoal powder, acrylic fibers, animal or plant fibers or a mixture of at least two selected from those ingredients. The tungsten powder may be replaced with titanium powder or a mixture of tungsten powder and titanium powder.

[0225] By processing the mixture of phenol resin, graphite powder and tungsten powder in a manner similar to that used for making Example 4, balls for light emitting heater of impermeability graphite of high density with a small number of pores were each made in the form of a sphere.

[0226] The balls, thus obtained, had excellent characteristics similar to those of the balls of Example 4, and a specific gravity of 1.5-1.8. It is to be noted that when tungsten powder having a specific gravity of  $9.0\text{ g/cm}^3$  (pressed under a pressure of 98 MPa) was used, the balls had a specific gravity of 2.66-2.7. In order to apply pressure to the balls to increase their density to thereby give impermeability to them, tungsten powder having a specific gravity of  $9.0\text{ g/cm}^3$  is preferably used.

(Example 6)

[0227] This Example is exactly the same as Example 1 except for the ingredients to be used. Thus, further description of the identical portions of Examples 1 and 6 will be omitted and only different portions of Example 6 from Example 1 will be described next.

[0228] Twenty weight parts of phenol resin, 10-20 weight parts of zirconium powder, and 60-70 weight parts of graphite powder (including 99.5 % of fixed carbon having an average grain size of 4 $\mu$ m) were mixed. Instead of phenol resin, a polydivinyl benzene resin may be used. The graphite powder may be replaced with carbon black powder, coke, charcoal powder such as Japanese Bincho charcoal powder, acrylic fibers, animal or plant fibers or a mixture of at least two selected from those ingredients.

[0229] A mixture of phenol resin, graphite powder and carbon fibers was then heated to 250-300 °C to cure the phenol resin, and burnt in the HIP at 1900 °C (higher than the melting point of 1857 °C of zirconium) to cause its carbon and zirconium to react with each other to form zirconium carbide (ZrC) (having a melting point of 3540 °C, a boiling point of 5100 °C and a Mohs' hardness of not lower than 8) of a high density with a small number of pores. It was then further burnt at 3000 °C in the HIP to produce balls for light emitting heater of impermeability graphite each in the form of a sphere. Since zirconium had a melting point of 1857 °C, the mixture was burnt in the HIP at 1900 °C higher than the melting point of zirconium. When another metal is used instead of zirconium, it is caused to react with carbide to form metal carbide. Thus, the half-finished products are preferably burnt in the HIP at a temperature of not lower than the melting point of the metal.

[0230] The balls, thus obtained, had excellent characteristics similar to those of the balls of Example 1 as well as excellent heat resistance due to addition of the zirconium powder.

[0231] When the amount of zirconium powder to be added is less than 10 weight parts, great improvements in the heat resistance of the balls cannot be expected whereas when it exceeds 20 weight parts, cracks are liable to occur in the balls as in Examples 4 and 5.

[0232] The zirconium powder may be replaced with niobium (Nb) or boron (B) powder or a mixture of at least two of those three materials. In addition, 10-20 weight parts of at least one of tungsten and titanium powder may be added. A total quantity of those metal ingredients should not exceed 40 weight parts. Forty weight parts or more of graphite (carbon black) powder and about 20 weight parts of phenol resin as a binder are preferably added.

[0233] When zirconium and niobium powder were together used, they reacted at high temperatures to produce a product of superconductivity. Niobium reacted with graphite (carbon black) powder to become niobium carbide which served to improve the heat resistance, hardness and electric conductivity of the resulting balls for light emitting heater.

[0234] While in the Examples described above the materials were illustrated as being heated in a mold and pressed into spheres, they may be heated in a capsule and pressed into a rod, which may then be cut away and then ground into spheres. In that case, the capsule which contains the materials is evacuated and heated to cure the phenol resin.

The temperature is then increased to 1900 °C or more to burn the capsule under a pressure of 49-294 MPa in the HIP, and further burnt at 3000 °C in the HIP.

[0235] Even before burning at 3000 °C, the rod includes a carbon material of a very high density. Thus, if this rod is cut away and then ground into spheres, those spheres are suitable for use as the balls for light emitting heater with a small number of pores.

[0236] Although in the case of the method of using the mold, two different steps which include molding the material into spheres and burning the material in the HIP are required to be performed. The method of using such capsule is only required to perform the HIP burning step, economically.

[0237] The material of the capsule is not especially limited as long as it does not react with the materials of the balls for light emitting heater at high temperature. Usually, stainless steel, aluminum and iron are named as the capsule material.

(Example 7)

[0238] An example of making balls for light emitting heater, using as a binder pitch (petroleum, coal tar or pine pitch), will be explained next.

[0239] Graphite powder (which may be replaced with carbon black powder), pitch, metal powder, and a smallest amount of solvent were mixed and then charged into a column-type capsule of stainless steel, aluminum or iron up to about 80 vol % of the capsule capacity. The capsule was then evacuated to a vacuum state and then burnt at 1000 °C, and further burnt at 1900 °C or more at a pressure of from 49 to 294 MPa for carbonizing purposes. It was then graphitized at 3000 °C, and then processed into the balls for light emitting heater of impermeability graphite of a high density with a small number of pores.

[0240] The quantity of graphite powder used was not less than 40 weight parts. The metal powder is at least one selected from the group of tungsten, titanium, zirconium, niobium and boron powder, and its total amount added was 10-20 weight parts.

[0241] Even before burning at 3000 °C, the rod includes a carbon material of a very high density. Thus, if this rod is cut away and then ground into spheres, those spheres are suitable for use as the balls for light emitting heater with a small number of pores.

(Example 8)

[0242] In the Examples 1-6 the pressurizing and burning steps were illustrated as being performed in the inert gas. If nitrogen gas is used as the inert gas, the added metal ingredients are nitrated. Thus, the strength, hardness and discharge resistance of the balls for light emitting heater are increased.

[0243] Similar effects were also obtained by again burning the balls for light emitting heater made in each of Examples 1-7 in a nitrogen gas atmosphere at 1900-2000 °C.

## 10 Claims

1. A thermal decomposition apparatus for wastes comprising:

a heating chamber for heating the wastes;  
 an inlet port for introducing the wastes into said heating chamber;  
 at least one pair of electrodes provided within said heating chamber;  
 a light emitting heater consisting a plurality of balls which contain carbon as a main ingredient, said light emitting heater being provided between said at least one pair of electrodes so as to produce an electric discharge when a voltage is applied across said at least one pair of electrodes; and  
 an outlet port for discharging out of said heating chamber gases into which the wastes are thermally decomposed.

2. The thermal decomposition apparatus according to claim 1, further comprising oxygenless state forming means for placing said heating chamber in an oxygenless state such that said plurality of balls are placed in an oxygenless state.

3. The thermal decomposition apparatus according to claim 1, further comprising decompressing means for decompressing said heating chamber such that said plurality of balls are placed in a vacuum state.

4. The thermal decomposition apparatus according to any one of claims 1 to 3, wherein said plurality of balls are each made of at least one selected from the group of charcoal, graphite and a carbon composite material.

5. The thermal decomposition apparatus according to any one of claims 1 to 3, wherein said plurality of plurality of balls each have impermeability.

6. The thermal decomposition apparatus according to any one of claims 1 to 3, wherein said plurality of balls each take the form of a perfect sphere.

7. The thermal decomposition apparatus according to any one of claims 1 to 3, further comprising pressing means provided within said heating chamber for pressing the wastes against said plurality of balls.

8. The thermal decomposition apparatus according to any one of claims 1 to 7, further comprising a filter made of at least one of activate carbon and charcoal for allowing the decomposed gases to pass therethrough.

9. The thermal decomposition apparatus according to any one of claims 1 to 3, further comprising a vacuum meter for measuring the pressure within said heating chamber, and pressure adjusting means for adjusting the pressure within said heating chamber to a predetermined value.

10. The thermal decomposition apparatus according to any one of claims 1 to 3, further comprising an intervening spacer which contain carbon as a main ingredient, the intervening spacer being placed at least between said plurality of balls and an inner wall of said heating chamber.

11. The thermal decomposition apparatus according to any one of claims 1 to 3, wherein at least portions of the inner wall of said heating chamber which are placed in contact with said plurality of balls is made of a monolithic refractory which contains at least one selected from the group of boron nitride, niobium, silicon carbide, boron carbide, magnesium oxide, hafnium oxide, hafnium dioxide, and beryllium aluminum oxide.

12. The thermal decomposition apparatus according to any one of claims 1 to 3, wherein at least a part of the pairs

of electrodes may take the form of a rod or horn surrounded by said plurality of balls.

13. The thermal decomposition apparatus according to any one of claims 1 to 3, further comprising a pipe for introducing liquid wastes into said heating chamber.

14. The thermal decomposition apparatus according to any one of claims 1 to 3, further comprising a decomposed gas harm eliminating device for thermally decomposing harmful materials remaining in the decomposed gases into harmless gases, the decomposed gas harm eliminating device comprising:

a decomposed gas heating chamber for heating the decomposed gases;  
a decomposed gas inlet port for introducing the decomposed gases into said decomposed gas heating chamber;  
at least one pair of second electrodes provided within said decomposed gas heating chamber;  
a second light emitting heater consisting of a plurality of second balls which contain carbon as a main ingredient, provided between said at least one pair of second electrodes so as to produce an electric discharge when a voltage is applied across said at least one pair of second electrodes; and  
a harmless gas outlet port for discharging out of said decomposed gas heating chamber harmless gases to which the decomposed gases are rendered harmless; and  
a filter comprising at least one of active carbon and charcoal for allowing the harmless gases pass therethrough.

15. The thermal decomposition apparatus according to claim 14,  
wherein said decomposed gas harm eliminating device further comprising at least one of:

a second vacuum meter for measuring the pressure within said decomposed gas heating chamber, and second pressure adjusting means for adjusting the pressure within said decomposed gas heating chamber to a predetermined value;  
a second intervening spacer which contain carbon as a main ingredient, placed at least between said plurality of second balls and the inner wall of said decomposed gas heating chamber;  
at least portions of the inner wall of said decomposed gas heating chamber which are placed in contact with said plurality of second balls being made of a monolithic refractory which contains at least one selected from the group of boron nitride, niobium, silicon carbide, boron carbide, magnesium oxide, hafnium oxide, hafnium dioxide, and beryllium aluminum oxide; and  
a second pair of electrodes having at least a part thereof in the form of a rod or horn surrounded by said plurality of second balls.

#### Amended claims under Art. 19.1 PCT

1. (Canceled)

2. (Amended) A thermal decomposition apparatus for wastes comprising:

a heating chamber for heating the wastes;  
an inlet port for introducing the wastes into said heating chamber;  
at least one pair of electrodes provided within said heating chamber;  
a light emitting heater consisting of a plurality of balls which contain carbon as a main ingredient, said light emitting heater being provided between said at least one pair of electrodes so as to produce an electric discharge when a voltage is applied across said at least one pair of electrodes; and  
an outlet port for discharging out of said heating chamber gases into which the wastes are thermally decomposed  
wherein said plurality of balls are placed in an oxygenless state..

2. (Amended) A thermal decomposition apparatus for wastes comprising:

a heating chamber for heating the wastes;  
an inlet port for introducing the wastes into said heating chamber;  
at least one pair of electrodes provided within said heating chamber;  
a light emitting heater consisting of a plurality of balls which contain carbon as a main ingredient, said light



emitting heaters being provided between said at least one pair of electrodes so as to produce an electric discharge when a voltage is applied across said at least one pair of electrodes; and an outlet port for discharging out of said heating chamber gases into which the wastes are thermally decomposed

wherein said plurality of balls are placed in a vacuum state.

4. (Amended) The thermal decomposition apparatus according to claim 2 or 3, wherein said plurality of balls are each made of at least one selected from the group of charcoal, graphite and a carbon composite material.

5. (Amended) The thermal decomposition apparatus according to claim 2 or 3, wherein said plurality of balls each have impermeability.

6. (Amended) The thermal decomposition apparatus according to claim 2 or 3, wherein said plurality of balls each take the form of a perfect sphere.

7. (Amended) The thermal decomposition apparatus according to claim 2 or 3, further comprising pressing means provided within said heating chamber for pressing the wastes against said plurality of balls.

8. (Amended) The thermal decomposition apparatus according to claim 2 or 7, further comprising a filter made of at least one of activate carbon and charcoal for allowing the decomposed gases to pass therethrough.

9. (Amended) The thermal decomposition apparatus according to claim 2 or 3, further comprising a vacuum meter for measuring the pressure within said heating chamber, and pressure adjusting means for adjusting the pressure within said heating chamber to a predetermined value.

10. (Amended) The thermal decomposition apparatus according to claim 2 or 3, further comprising an intervening spacer which contain carbon as a main ingredient, the intervening spacer being placed between said plurality of balls and an inner wall of said heating chamber.

11. (Amended) The thermal decomposition apparatus according to claim 2 or 3, wherein at least portions of the inner wall of said heating chamber which are placed in contact with said plurality of balls is made of a monolithic refractory which contains at least one selected from the group of boron nitride, niobium, silicon carbide, boron carbide, magnesium oxide, hafnium oxide, hafnium dioxide, and beryllium aluminum oxide.

12. (Amended) The thermal decomposition apparatus according to claim 2 or 3, wherein at least a part of the pairs of electrodes may take the form of a rod or horn surrounded by said plurality of balls.

13. (Amended) The thermal decomposition apparatus according to claim 2 or 3, further comprising a pipe for introducing liquid wastes into said heating chamber.

14. (Amended) The thermal decomposition apparatus according to claim 2 or 3, further comprising a decomposed gas harm eliminating device for thermally decomposing harmful materials remaining in the decomposed gases into harmless gases, the decomposed gas harm eliminating device comprising:

- a decomposed gas heating chamber for heating the decomposed gases;
- a decomposed gas inlet port for introducing the decomposed gases into said decomposed gas heating chamber;
- at least one pair of second electrodes provided within said decomposed gas heating chamber;
- a second light emitting heater consisting of a plurality of second balls which contain carbon as a main ingredient, provided between said at least one pair of second electrodes so as to produce an electric discharge when a voltage is applied across said at least one pair of second electrodes; and
- a harmless gas outlet port for discharging out of said decomposed gas heating chamber harmless gases to which the decomposed gases are rendered harmless; and
- a filter comprising at least one of active carbon and charcoal for allowing the harmless gases pass therethrough.

15. The thermal decomposition apparatus according to claim 14, wherein said decomposed gas harm eliminating device further comprising at least one of:

a second vacuum meter for measuring the pressure within said decomposed gas heating chamber, and second pressure adjusting means for adjusting the pressure within said decomposed gas heating chamber to a pre-determined value;

a second intervening spacer which contain carbon as a main ingredient, placed at least between said plurality of second balls and the inner wall of said decomposed gas heating chamber;

at least portions of the inner wall of said decomposed gas heating chamber which are placed in contact with said plurality of second balls being made of a monolithic refractory which contains at least one selected from the group of boron nitride, niobium, silicon carbide, boron carbide, magnesium oxide, hafnium oxide, hafnium dioxide, and beryllium aluminum oxide; and

a second pair of electrodes having at least a part thereof in the form of a rod or horn surrounded by said plurality of second balls.

FIG. 1

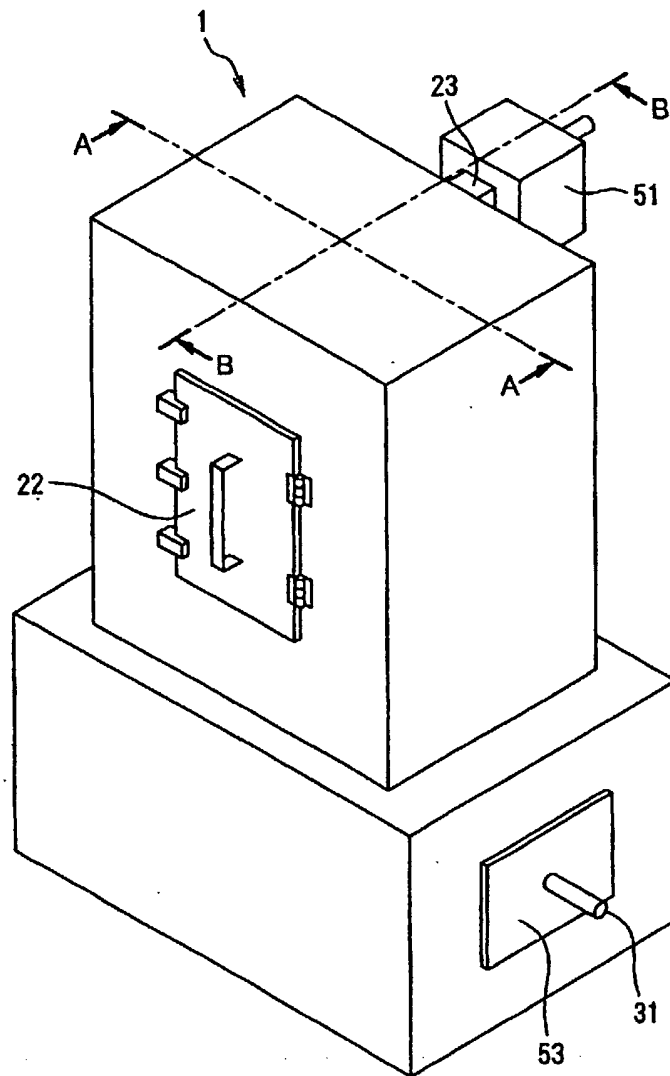


FIG. 2

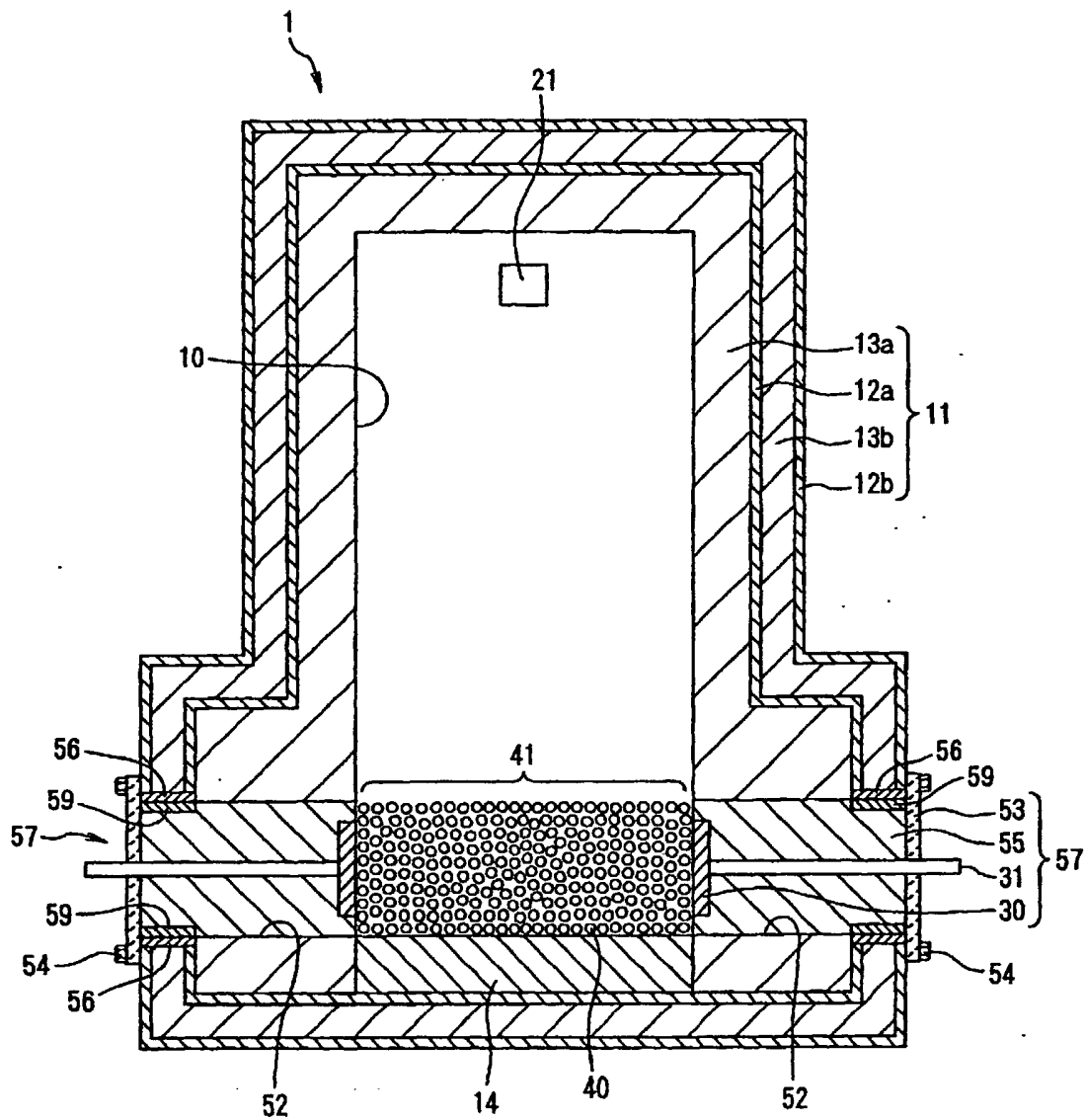


FIG. 3

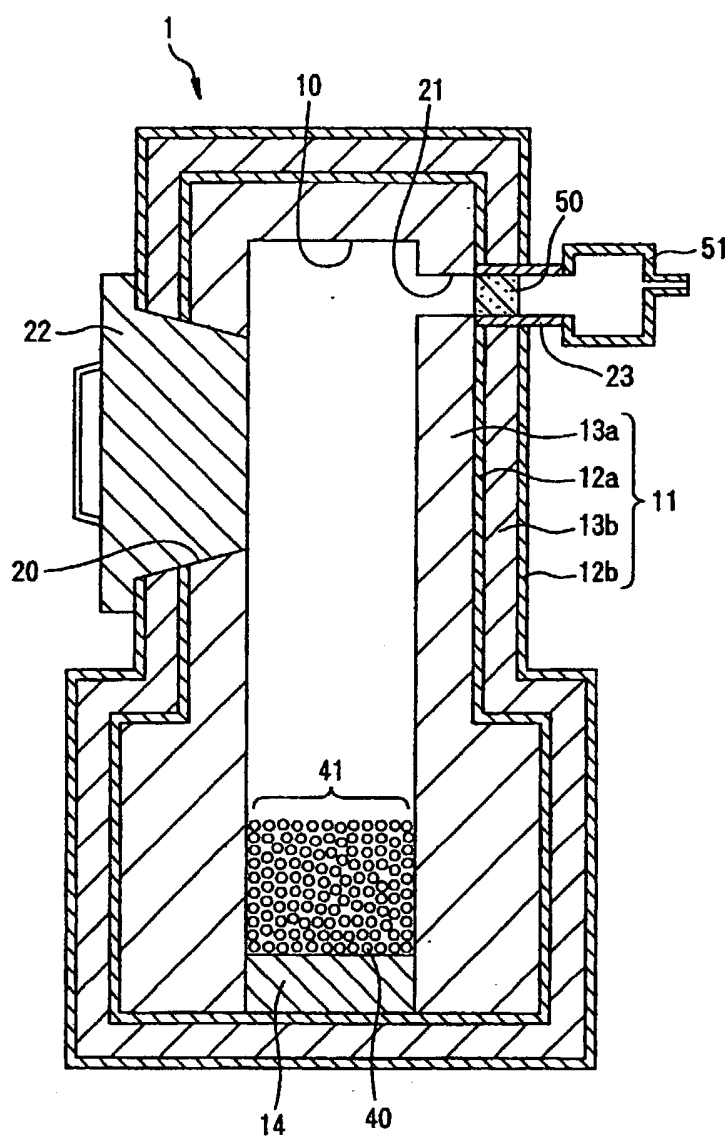


FIG. 4 (a)

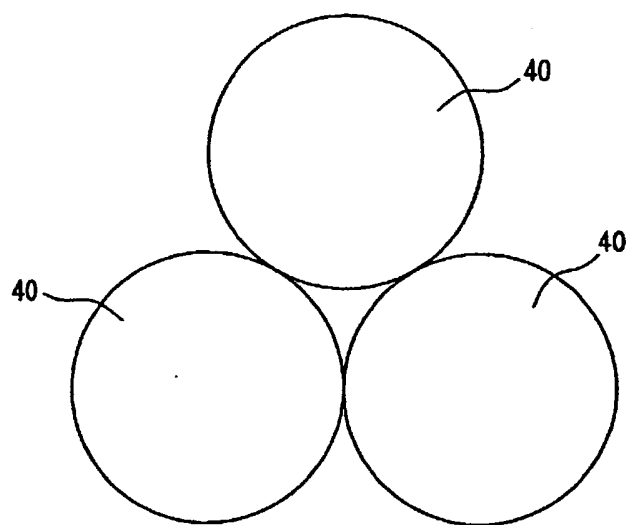


FIG. 4 (b)

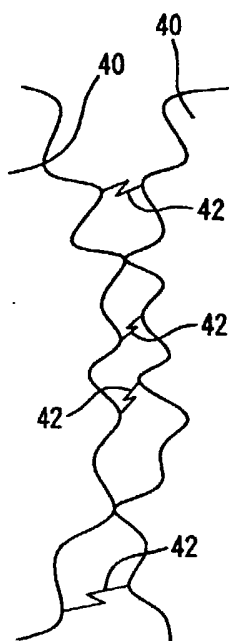


FIG. 5

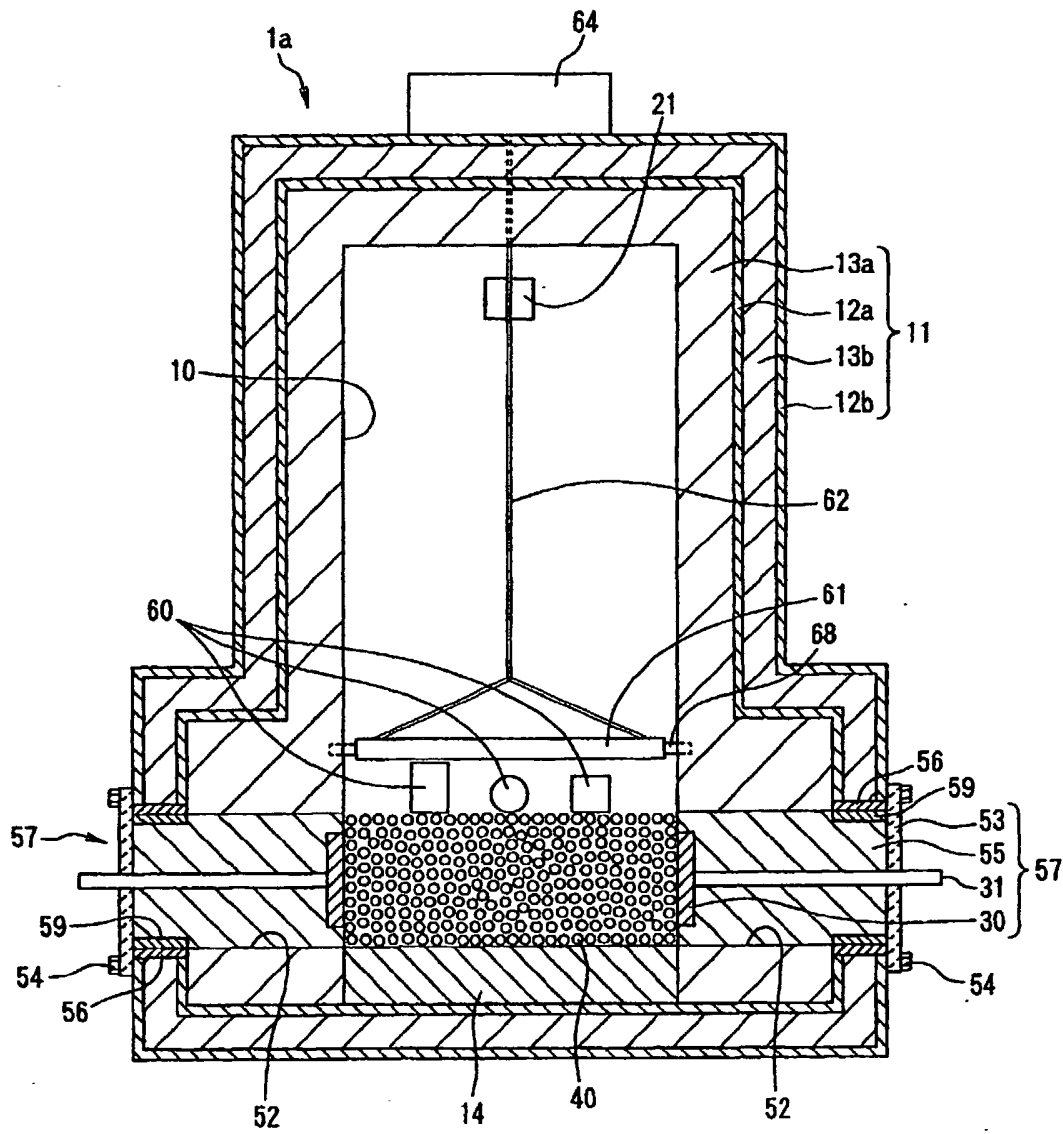


FIG. 6

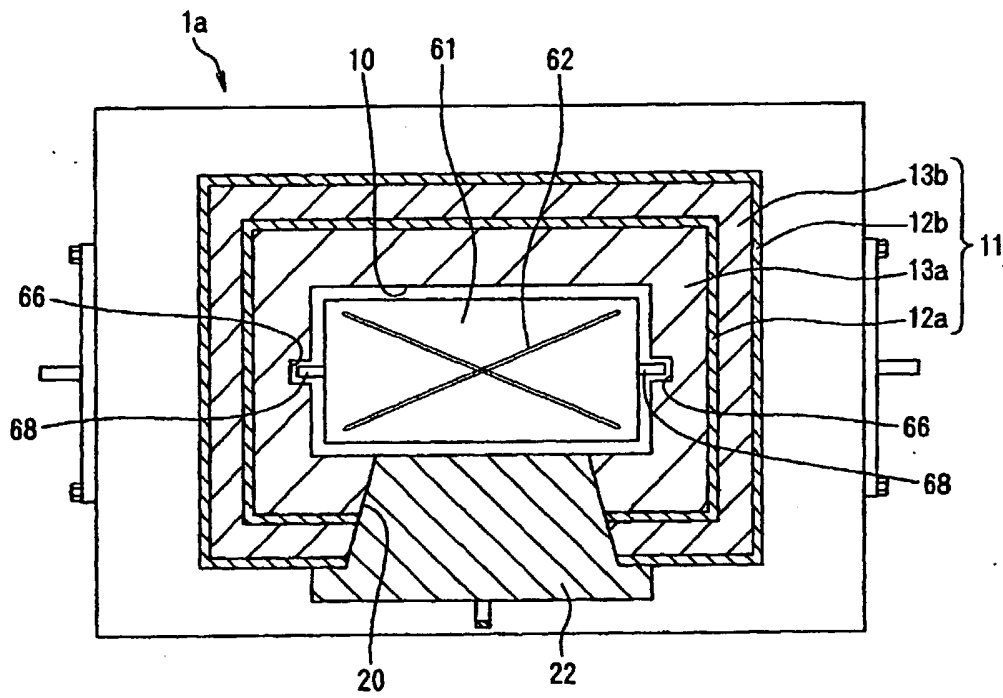




FIG. 7

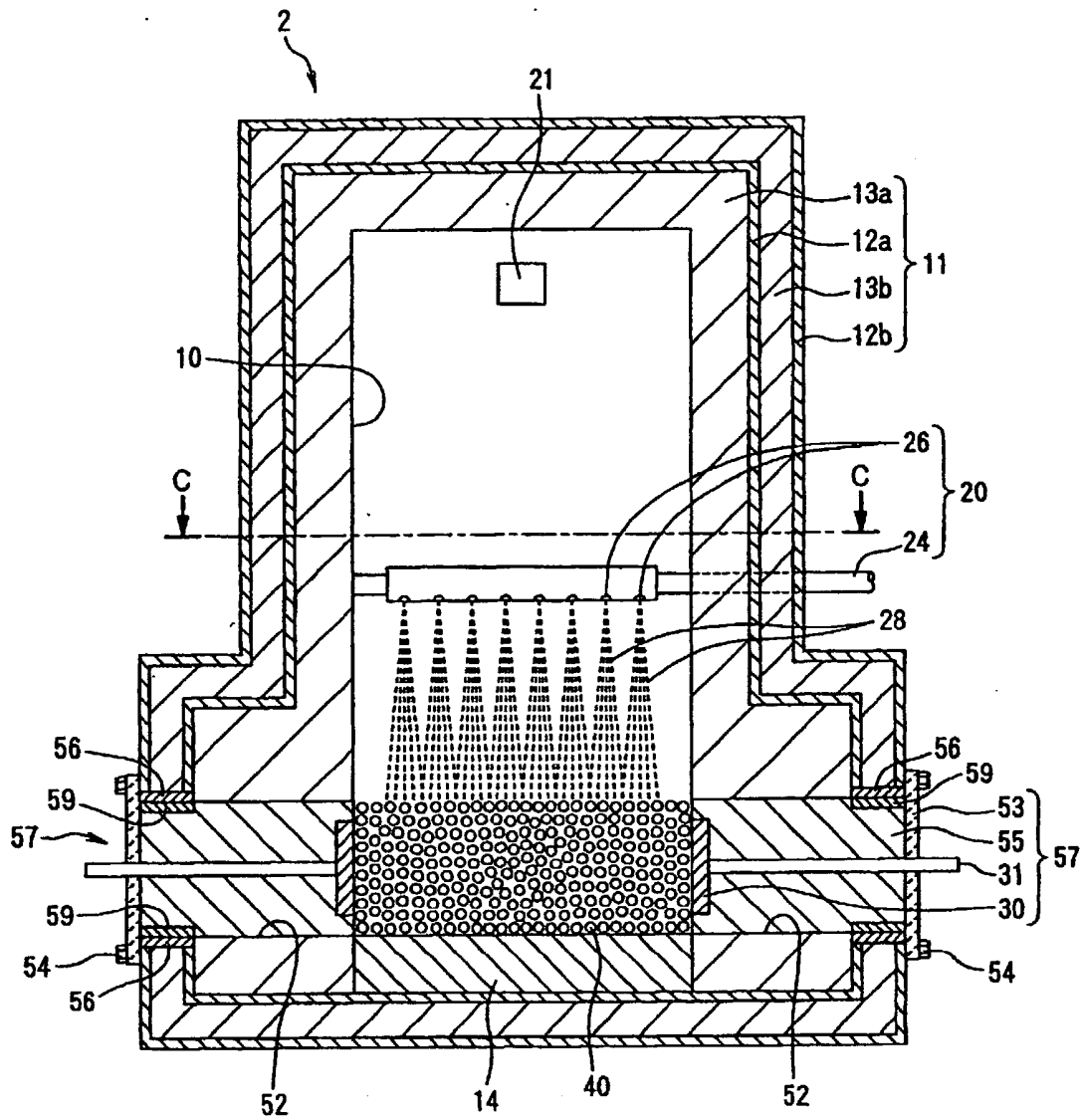


FIG. 8

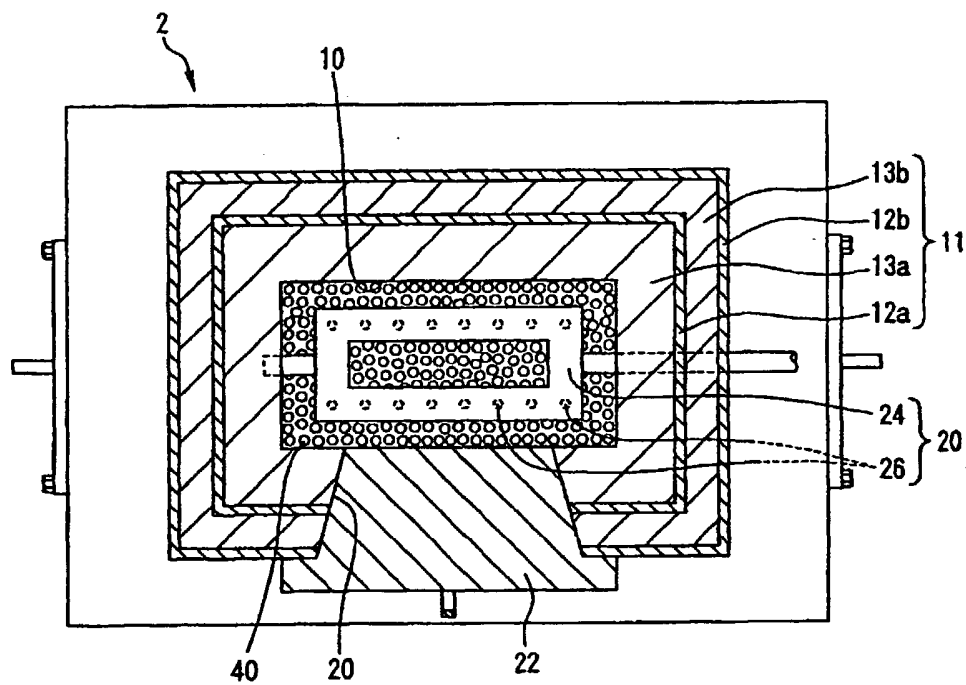


FIG. 9

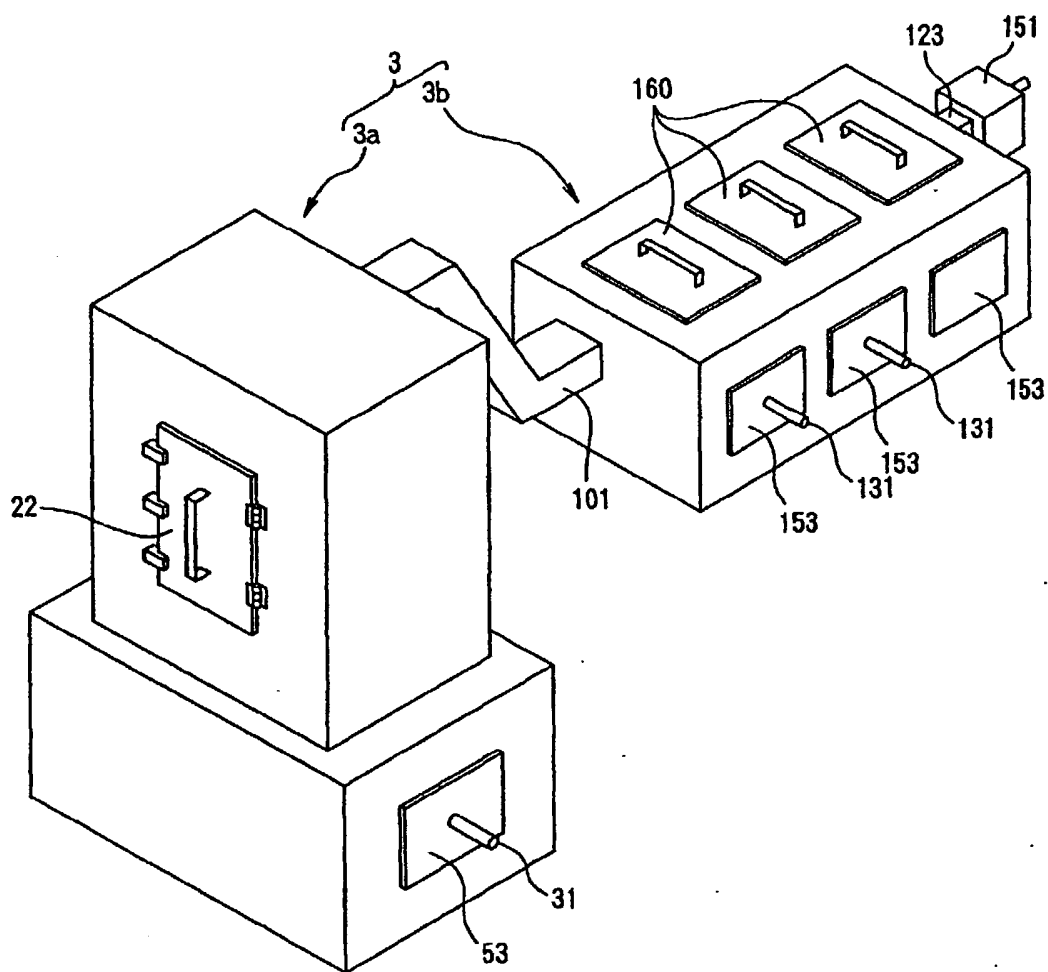


FIG. 10

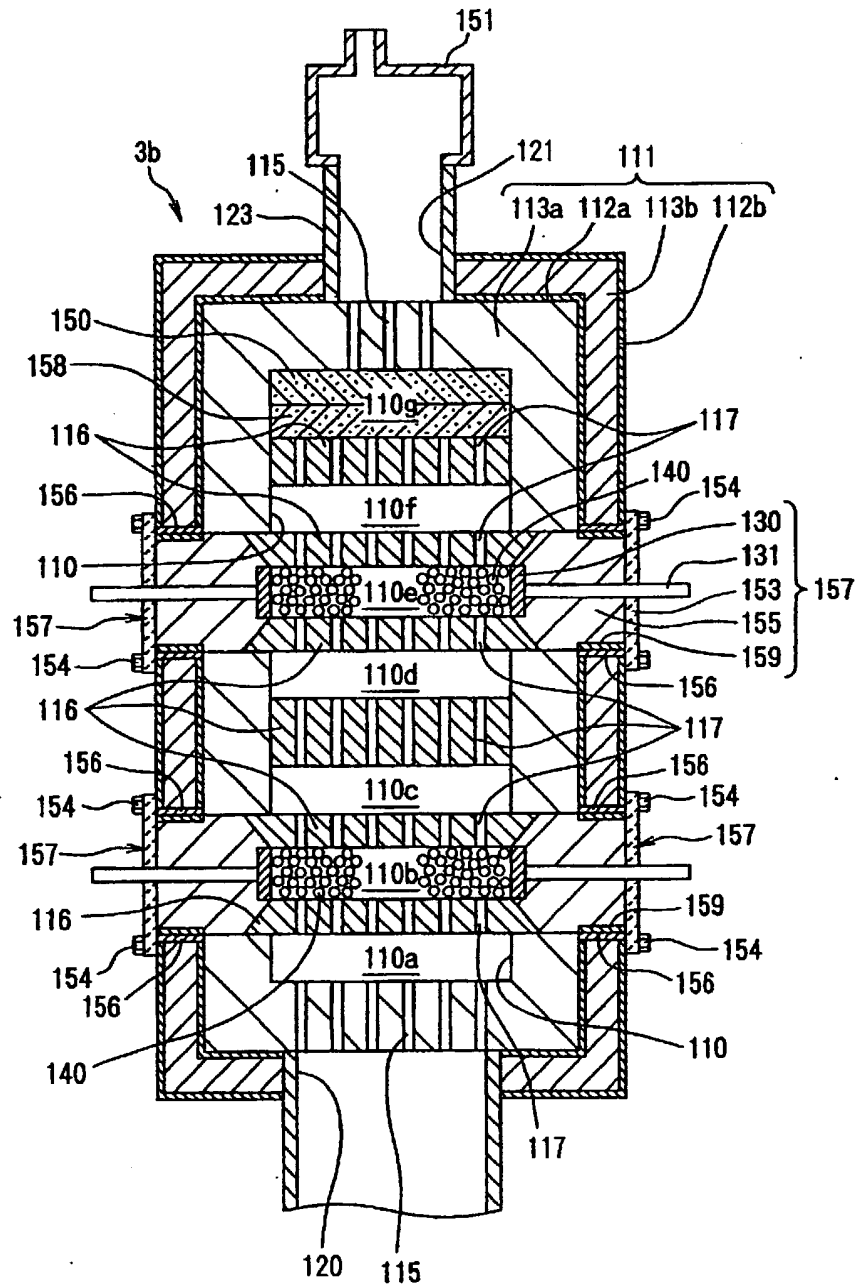


FIG. 11

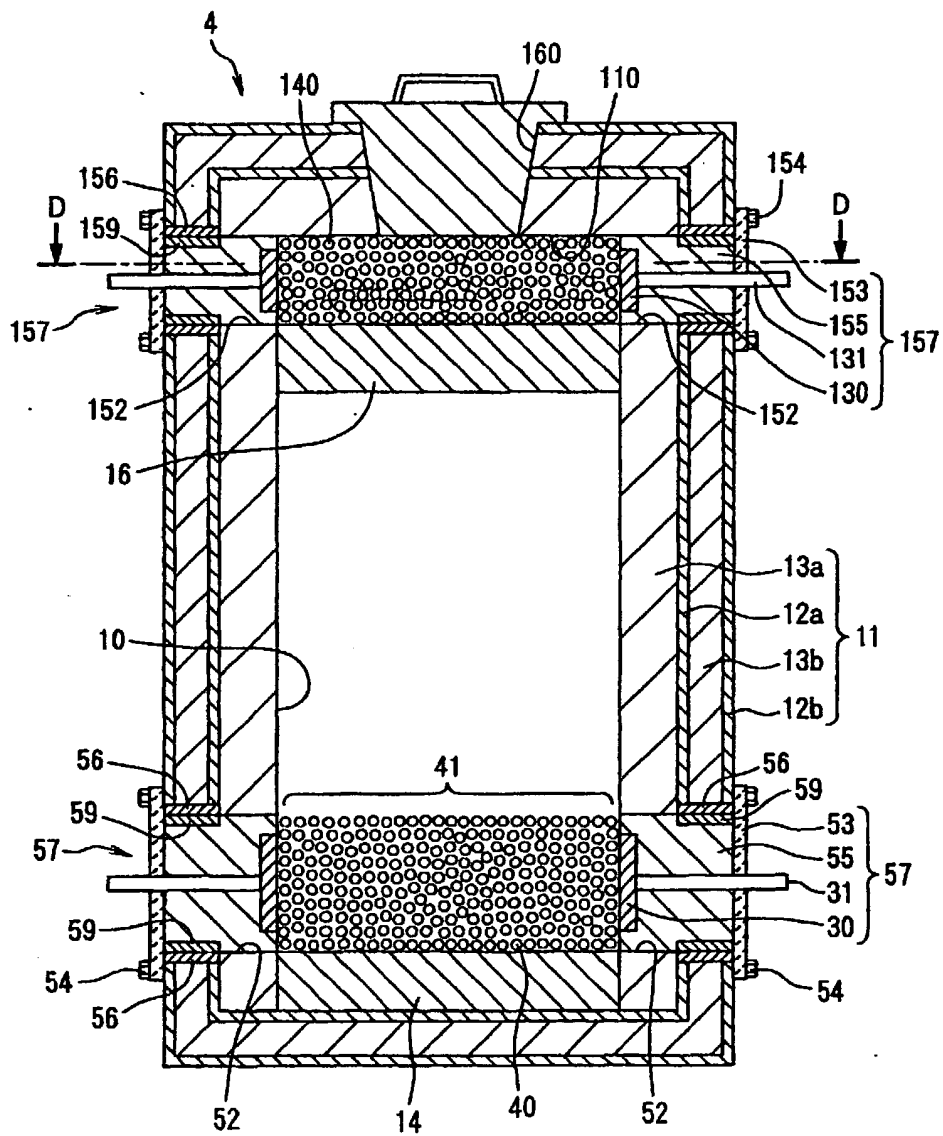


FIG. 12

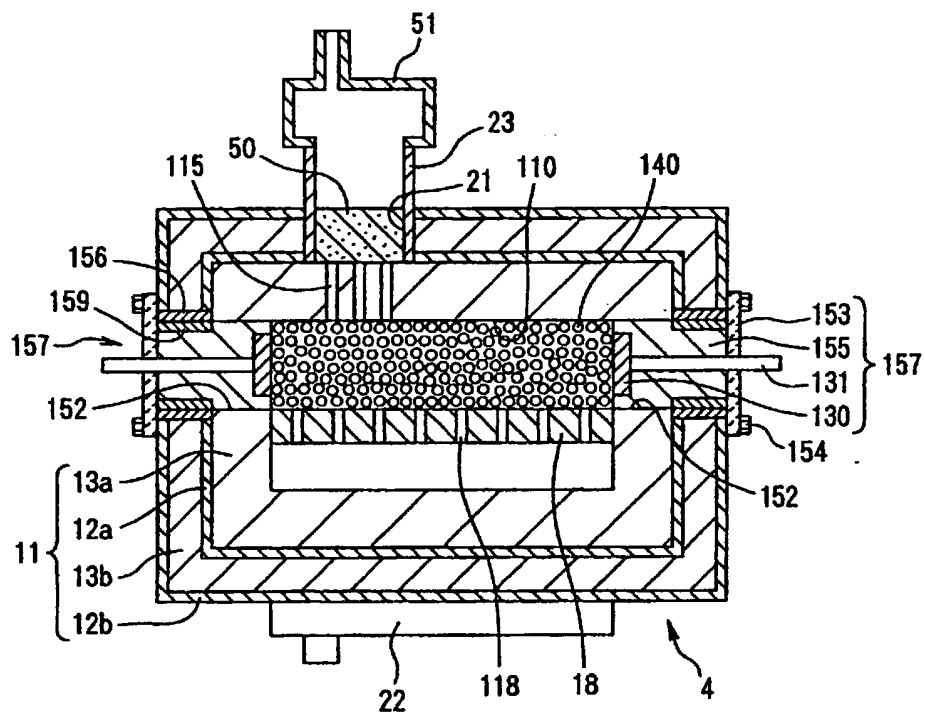


FIG. 13

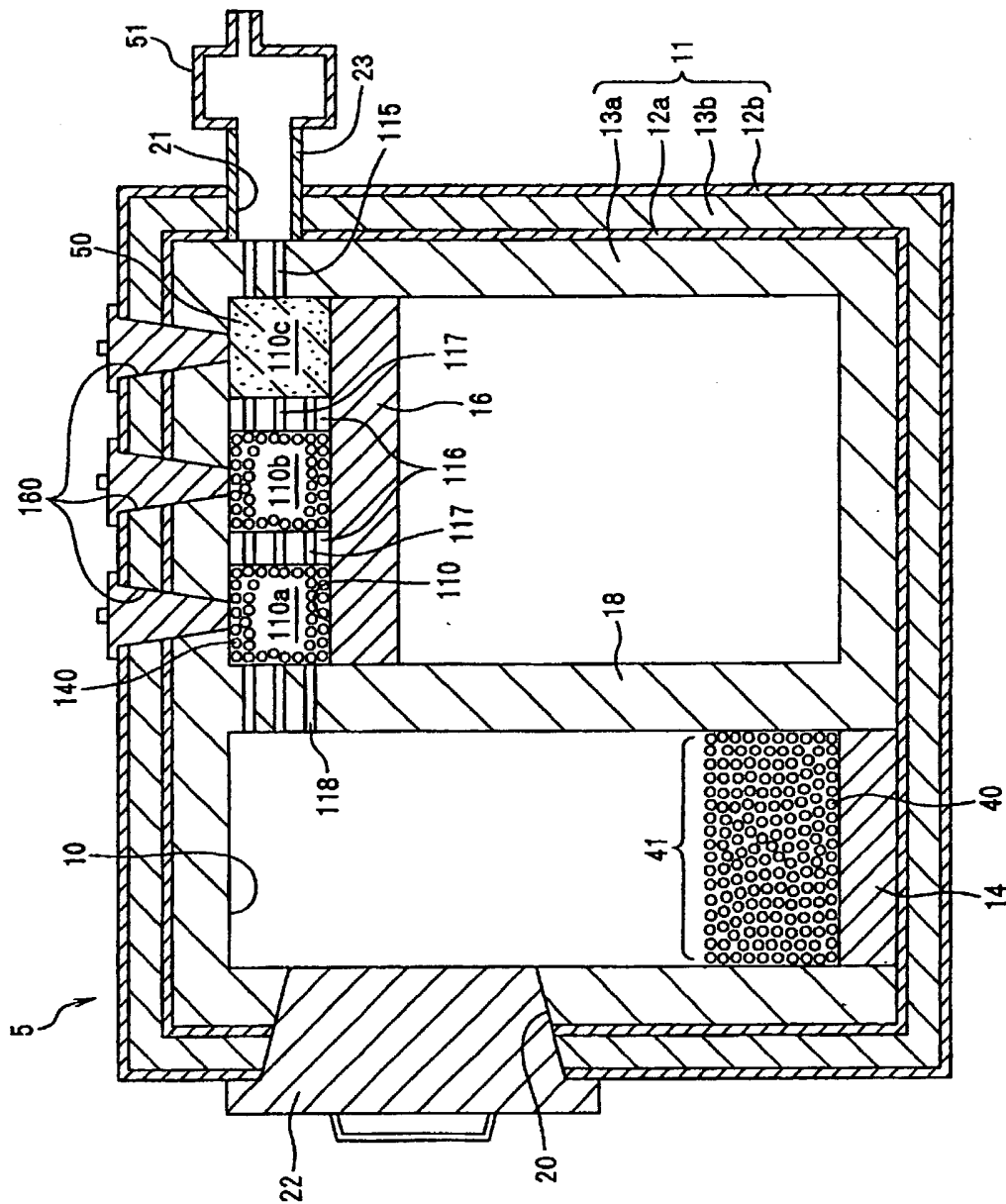


FIG. 14 (a)

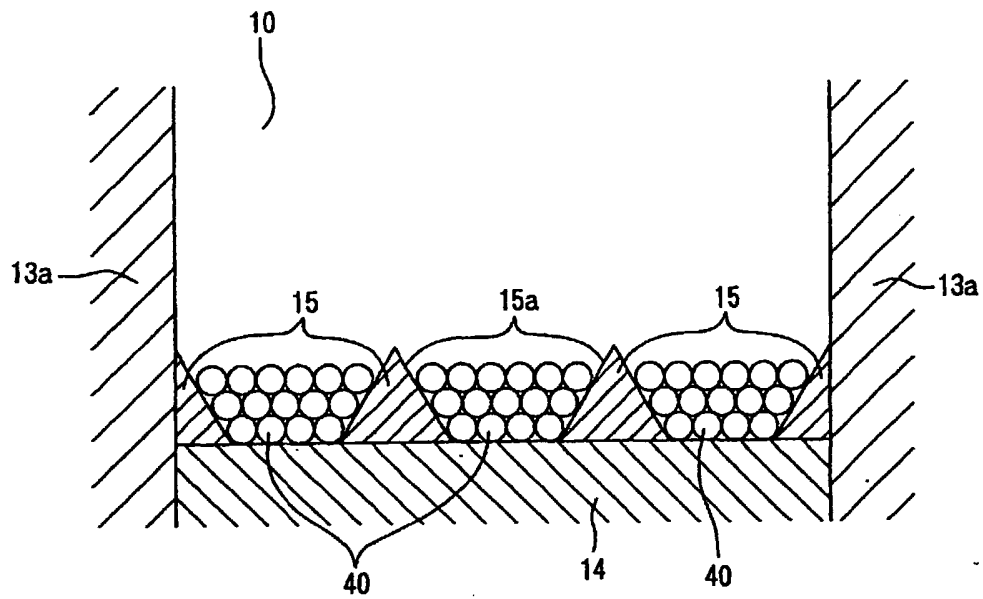


FIG. 14 (b)

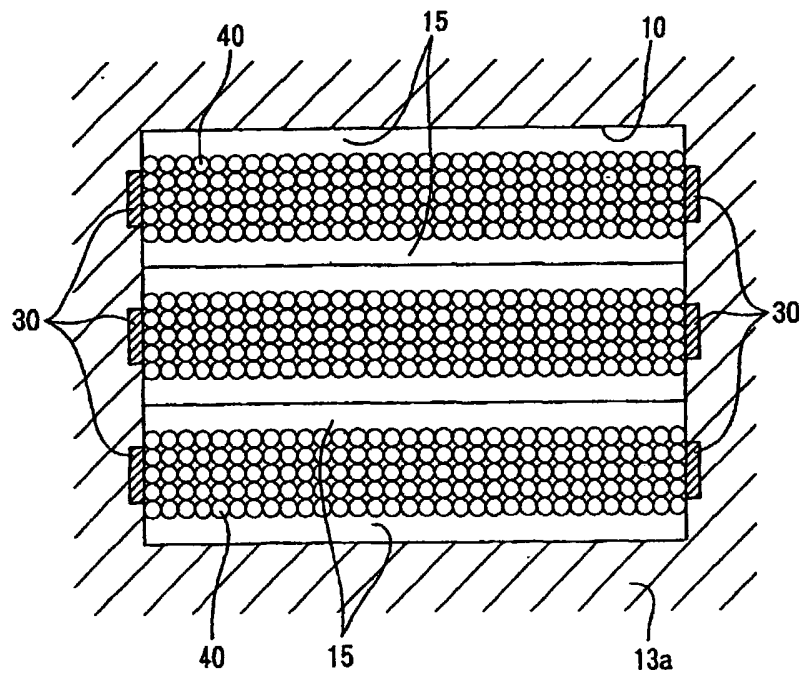




FIG. 15

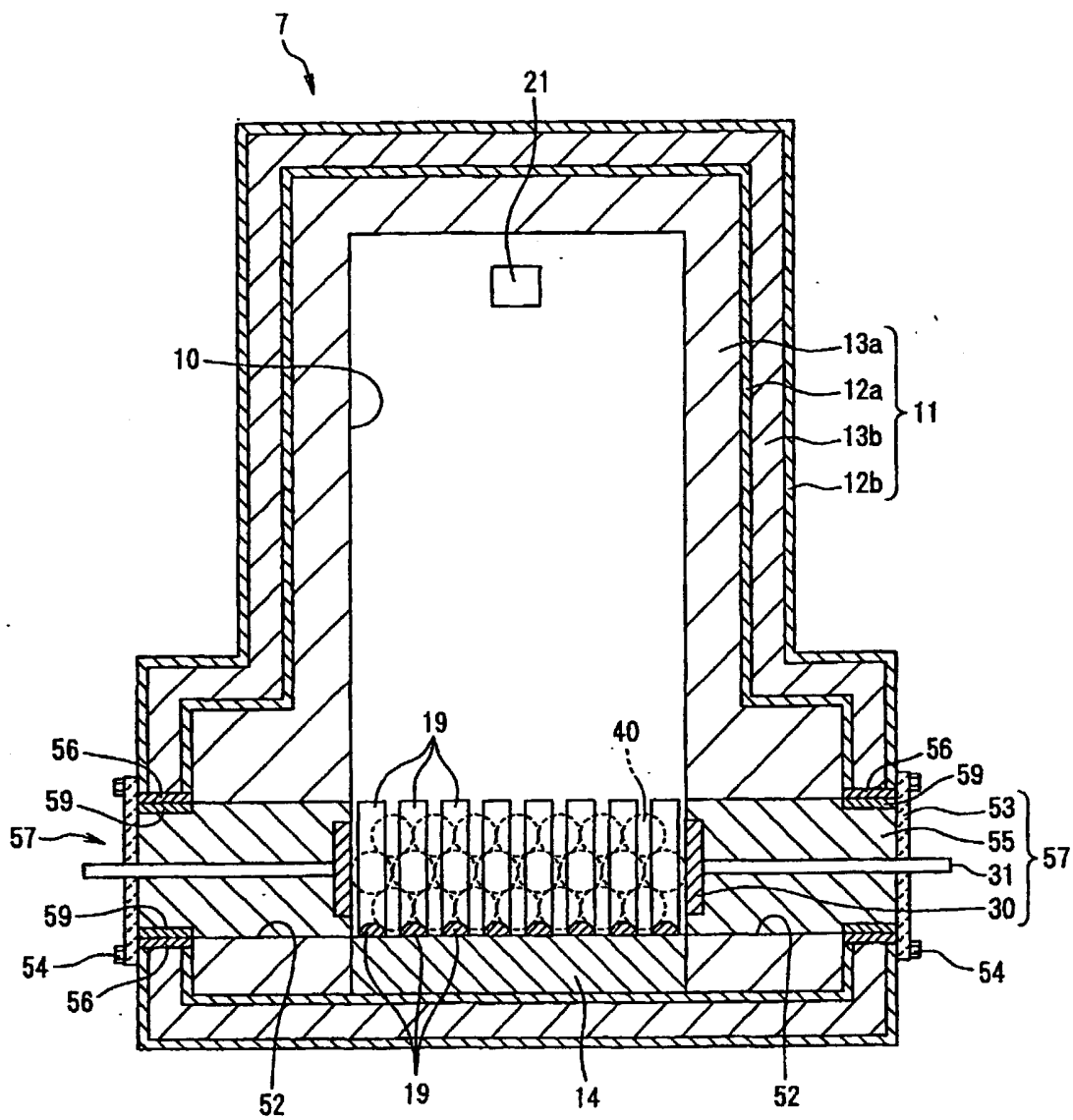


FIG. 16

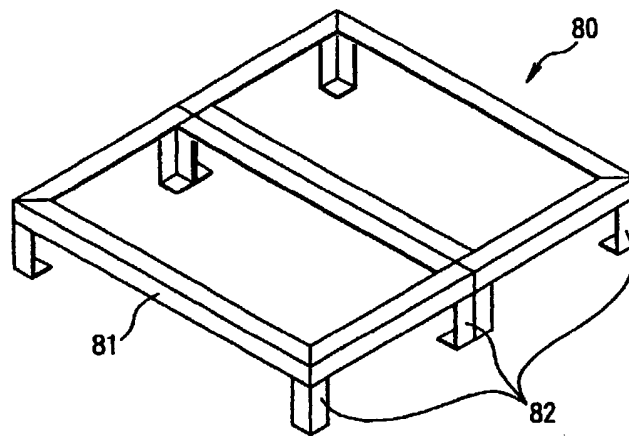


FIG. 17 (a)

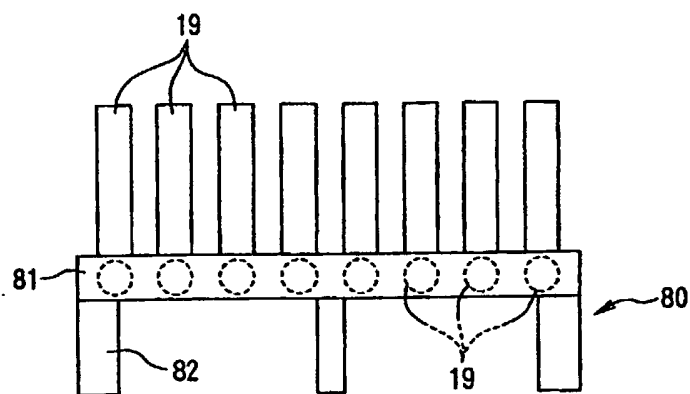


FIG. 17 (b)

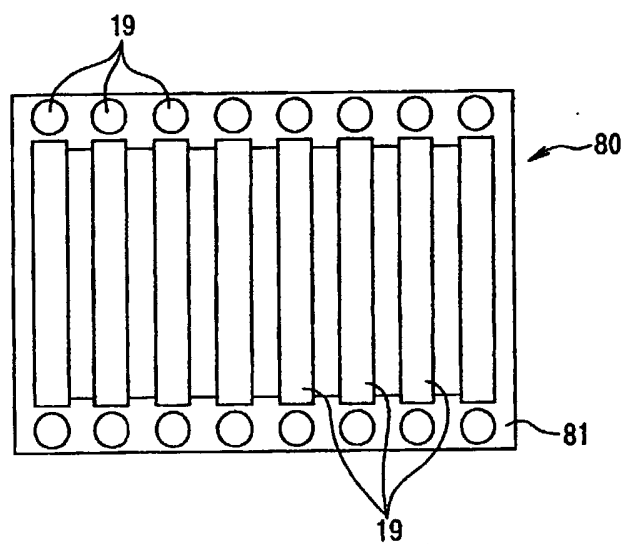
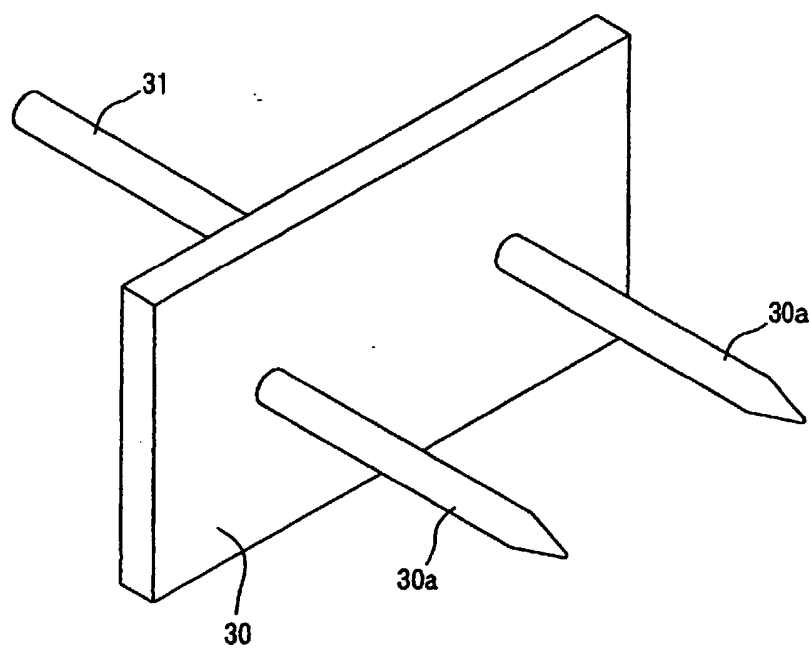


FIG. 18



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/00943

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl.<sup>7</sup> B09B3/00, F23G5/027, C10B53/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl.<sup>7</sup> B09B3/00, F23G5/027, C10B53/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1926-1996	Toroku Jitsuyo Shinan Koho	1994-1999
Kokai Jitsuyo Shinan Koho	1971-1999	Jitsuyo Shinan Keisai Koho	1996-1999

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPIL(DIALOG)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 10-36851, A (Daiichi K.K.), 10 February, 1998 (10.02.98), Claims; Column 2, lines 4 to 14; Column 3, lines 47 to 50; Column 4, line 43 to Column 5, line 1 (Family: none)	1, 4-6, 8, 11, 14
EX	JP, 2000-121018, A (Kabushiki Kaisha SUZUKI DENSHI KIKI), 28 April, 2000 (28.04.00), Claims (Family: none)	1, 4-6
A	JP, 9-236239, A (Hitachi, Ltd.), 09 September, 1997 (09.09.97), Claims (Family: none)	1-15

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

## \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

Date of the actual completion of the international search

15 May, 2000 (15.05.00)

Date of mailing of the international search report

30.05.00

Name and mailing address of the ISA/  
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

12 **EUROPÄISCHE PATENTANMELDUNG**

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 15.03.89 Patentblatt 89/11

84 Benannte Vertragsstaaten:  
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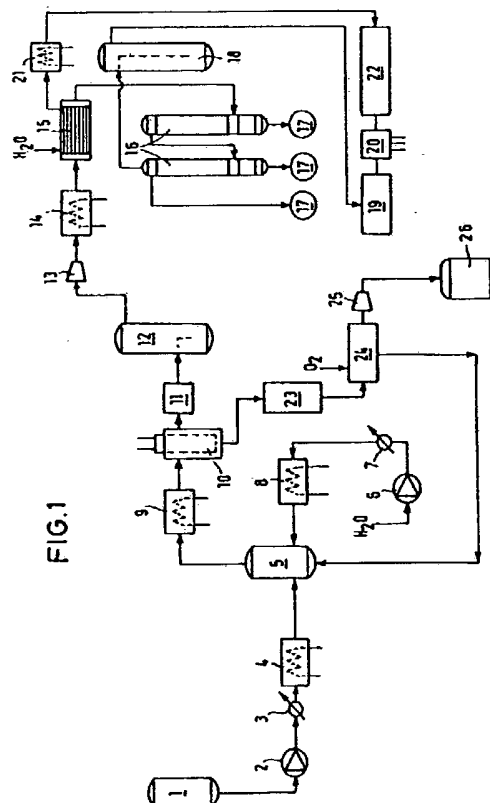
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54 **Verfahren und Anlage zur Energiegewinnung aus giftigen Abfallstoffen bei deren gleichzeitiger Entsorgung.**

57 Bei einem Verfahren zur Energiegewinnung aus giftigen Abfallstoffen bei deren gleichzeitiger Entsorgung, wobei die Abfallstoffe zumindest erhebliche Anteile von substituierten Kohlenwasserstoffen aufweisen wird vorgeschlagen, daß der Abfallstoff in einem beheizbaren Reaktor in Anwesenheit eines schwer verhüttbaren Metalloxides und eines elektrisch leitfähigen Materials, beispielsweise Elektrodenkoks oder Elektrographit, sowie im Kontakt mit Wasserdampf thermisch zersetzt wird, wobei eine dem Chlorgehalt der Abfallstoffe entsprechende Metalloxidmenge in flüchtiges Metallchlorid sowie ein Anteil freier Kohlenstoff in Kohlenmonoxid und ein mit dem Metalloxid nicht reagierender Anteil des Kohlenstoffs mit Hilfe einer stöchiometrischen Menge Wasserdampf zu Wassergas,  $\text{CO} + \text{H}_2$ , umgesetzt wird.



**"Verfahren und Anlage zur Energiegewinnung aus giftigen Abfallstoffen bei deren gleichzeitiger Entsorgung"**

Die Erfindung betrifft Verfahren zur Energiegewinnung aus giftigen Abfallstoffen bei deren gleichzeitiger Entsorgung, wobei die Abfallstoffe zumindest erhebliche Anteile von substituierten Kohlenwasserstoffen aufweisen, wie sie beispielsweise als Chlorverbindungen bzw. Chlorkohlenwasserstoffe der Formeln  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{C}_2\text{H}_2\text{Cl}_4$ , PCB, PVC, Polyvinylidenchlorid etc. vorliegen sowie zur Durchführung des Verfahrens geeignete Anlagen.

Substituierte, insbesondere halogenierte Kohlenwasserstoffe, wie sie beispielsweise im Tetrachlorkohlenstoff, Chloroform, Methylenchlorid, Tetra- und Trichloräthylen, Tetrachloräthan, PCB etc. aber auch im PVC oder Polyvinylidenchlorid vorliegen, sind insbesondere dann, wenn sie ihren Zweck erfüllt haben, ein mehr oder weniger problematischer Gift- oder Sondermüll, dessen man sich auf die verschiedenartigste Weise zu entledigen trachtet. Die Beseitigung erfolgt entweder durch Deponierung oder durch Verbrennung auf hoher See oder auch auf dem Lande in Hochtemperaturöfen mit einem Überschuß an Luft unter Energiezufuhr.

Der Energiebedarf ist in vielen Fällen nicht unerheblich, da nicht nur die zu beseitigenden Stoffe verdampft und auf die erforderliche Zersetzungstemperatur erhitzt, sondern auch enorme Luftmengen aufgeheizt werden müssen. Dabei wird entweder, wie bei der Verbrennung auf hoher See, eine Verschmutzung der Atmosphäre und die Gefahr sauren Regens in Kauf genommen oder es werden äußerst kostspielige Anlagen zur Luftreinigung erforderlich.

Die vorliegende Erfindung geht von der Aufgabe aus, mit einfachen Mitteln, Sonder- und Giftmüll, der substituierte, insbesondere halogenierte Kohlenwasserstoffe enthält, ohne Beeinflussung der Umwelt so umzuwandeln, daß industriell verwertbare Stoffe, z.B. Chlor und Brennstoffe entstehen. Zur Lösung dieser Aufgabe wird bei einem Verfahren zur Energiegewinnung aus substituierten Kohlenwasserstoffen, wie sie z.B. als  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{C}_2\text{H}_2\text{Cl}_4$ , PCB, PVC, Polyvinylidenchlorid etc. in reiner oder gebundener Form vorliegen, mit der Erfindung vorgeschlagen, daß der Abfallstoff in einem beheizbaren Reaktor in Anwesenheit eines schwer verhüttbaren Metalloxides und eines elektrisch leitfähigen Materials, beispielsweise Elektrodenkoks oder Elektrographit, sowie im Kontakt mit Wasserdampf thermisch zersetzt wird, wobei eine dem Chlorgehalt der Abfallstoffe entsprechende Metalloxidmenge in flüchtiges Metallchlorid sowie ein Anteil freiwerdenden Kohlenstoffs in Kohlen-

monoxid und ein mit dem Metalloxid nicht reagierender Anteil des Kohlenstoffs mit Hilfe einer stöchiometrischen Menge Wasserdampf zu Wassergas,  $\text{CO} + \text{H}_2$ , umgesetzt wird. Zu diesem Zweck werden die zu entsorgenden substituierten Kohlenwasserstoffe in festem, beispielsweise pulverisiertem, flüssigem oder gasförmigem Aggregatzustand in einen Induktionsofen eingetragen, der ein Gemisch aus Kohlenstoff, beispielsweise Koks, und schwer verhüttbarem Metalloxid, beispielsweise  $\text{Al}_2\text{O}_3$ , enthält und zusätzlich mit Wasserdampf beaufschlagt wird.

Anstelle oder zusätzlich zum beispielhaft angegebenen Metalloxid  $\text{Al}_2\text{O}_3$  können auch andere Metalloxide und / oder Metalloxyde bzw. Metallhydroxide enthaltende Stoffe wie Filterstäube, Flugaschen, Flugsande, Haldenberge, Galvanikschlämme und dergleichen zur Durchführung des Verfahrens zumindest anteilig verwendet werden.

Durch die erfindungsgemäße Lösung, wobei die zu entsorgenden substituierten Kohlenwasserstoffe unter Erhitzung im Kontakt mit Metalloxid sowie elektrisch leitfähigem Material und einer stöchiometrisch dosierten Menge Wasserdampf umgesetzt werden, wird erreicht, daß ausschließlich solche Umwandlungsprodukte bzw. Gase entstehen, die im weiteren Verlauf des Prozesses als chemisch weiterverwertbare Grundstoffe zur Herstellung von Folgeprodukten mit Vorteil verwendbar sind.

So wird beispielsweise aus dem in den substituierten Kohlenwasserstoffen enthaltenen Kohlenstoff gasförmiges Kohlenmonoxid freigesetzt, der gebundene Wasserstoff entweicht mit diesem zusammen als Wasserstoffgas und Chlor verbindet sich mit Metalloxid zu Metallchlorid, das bei der Umwandlungstemperatur im Reaktor flüchtig ist und vom übrigen Gas nach Abkühlung an geeigneter Stelle in einer Kondensationsstufe als Sublimat oder Kondensat ausgeschieden wird.

Ein weiterer Vorteil ergibt sich daraus, daß für bisher mit wirtschaftlichen Mitteln für nicht verhüttbar angesehene und daher mit Kosten zu entsorgende, Metalloxyde enthaltende umweltgefährdende Stoffe nunmehr mit der Erfindung eine wirtschaftlich nutzbringende Anwendung aufgezeigt wird.

Da bei den substituierten Kohlenwasserstoffen das Kohlenstoff-Wasserstoff-Verhältnis zugunsten des Kohlenstoffs verschoben ist, entstehen Wassergasgemische mit einem Unterschuß an Wasserstoff und einem Überschuß an CO. Durch Zugabe von definierten Mengen an Wasserdampf wird erreicht, daß entweder ein Wassergas mit ungefähr gleichen Anteilen an CO und  $\text{H}_2$  oder einem CO-

Volumenanteil entsteht, der doppelt so groß ist wie das Wasserstoffvolumen. Durch diese Maßnahme kann das entstandene Gasgemisch, das nach Abgabe seiner Wärmeenergie in einem Gasometer gesammelt wird, in der nachgeschalteten Fischer-Tropsch-Synthese nach einer der Idealgleichungen reagieren und ein Optimum an flüssigen Kohlenwasserstoffen liefern.

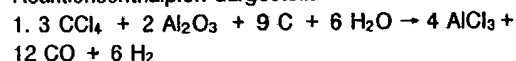
Die ebenfalls flüchtigen Chloride, beispielsweise  $\text{AlCl}_3$ ,  $\text{TiCl}_4$  etc. sublimieren an den dafür vorgesehenen Stellen und werden nach Umsetzung mit Sauerstoff bzw. durch einen nachgeschalteten, modifizierten Deacon-Prozeß wieder in die Metalloxide überführt und erneut in den Verfahrensgang eingeschleust. Dadurch ist es möglich, mit einer vergleichsweise geringen im Kreislauf geführten Menge Metalloxid vergleichsweise sehr große Mengen von substituierten Kohlenwasserstoffen zu entsorgen bzw. zu chemisch weiterverwertbaren Grundstoffen umzusetzen.

Das bei der Umsetzung der Chloride mit Sauerstoff entstandene Chlor kann industriell verwertet werden. So kann beispielsweise Rotschlamm, ein Abfallprodukt der Aluminiumindustrie, das bis heute kaum genutzt werden kann, in leicht trennbare Metallchloride überführt werden, die entweder als solche oder nach Umwandlung in die Oxide in verschiedenen Wirtschaftszweigen Verwendung finden können.

Bei der Bildung nutzbarer Kohlenwasserstoffe durch die nachgeschaltete Fischer-Tropsch-Synthese wird, da es sich um exotherme Reaktionen handelt, eine erhebliche Wärmemenge frei, die mit Hilfe von Kühlwasser abgeführt werden muß. Dadurch erhält man Wasserdampf, mit dessen Hilfe Turbinen, Dampfmotore etc. angetrieben werden können.

#### Ausführungsbeispiel A

Als erstes Ausführungsbeispiel der Erfindung sei die Energieerzeugung aus Tetrachlorkohlenstoff anhand der zugehörigen Reaktionsgleichungen und Reaktionsenthalpien dargestellt:



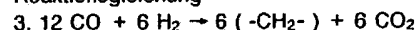
Aus den Bildungsenthalpien der einzelnen Reaktanden ergibt sich in erster Näherung die Reaktionsenthalpie:

$$2. \quad \Delta H = (4 \times -705,5 + 12 \times -110,5) - (3 \times -106,7 + 2 \times -1675 + 6 \times -236)$$

$$\Delta H = + 938,1 \text{ kJ/Formelumsatz}$$

Das bedeutet, daß für die Vernichtung von einer Tonne Tetrachlorkohlenstoff zunächst einmal 564 kWh und ca. 234 kg Kohlenstoff aufgewandt werden müssen. Verbrennt man das entstandene Gasgemisch von CO und  $\text{H}_2$  in einem Gasmotor

bei einem thermischen Wirkungsgrad von 34% und stellt elektrische Energie her, so erhält man ca. 983 kWh und eine Wärmeenergie von etwa 6.850.000 kJ. Benutzt man das entstandene Wassergas, - ein Gemisch von CO und  $\text{H}_2$ , wird als Wassergas bezeichnet -, zur Herstellung von brennbaren Kohlenwasserstoffen, Methan, Propan, Butan, etc. sowie den weiteren Homologen, die als Benzin, Dieselöl usw. technisch genutzt werden, in der Fischer-Tropsch-Synthese, so erhält man nach der Reaktionsgleichung



pro Tonne  $\text{CCl}_4$  ca. 180 kg nutzbare Kohlenwasserstoffe, von denen etwa 53% als Benzin verwendet werden können, während 34% als Gase und der Rest als Dieselöl und Paraffine anfallen.

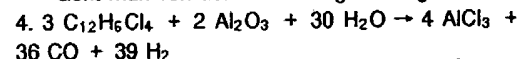
Die gleichzeitig auftretende Wärmeenergie von etwa 2.600.000 kJ muß durch Kühlwasser abgeführt werden und liefert einen Wasserdampf mit einem Druck von ungefähr 45 - 48 bar. Mit Hilfe eines Dampfmotors kann daraus bei einem Wirkungsgrad von 25% elektrische Energie von ca. 180 kWh erzeugt werden. Setzt man die gasförmigen Kohlenwasserstoffe, die der Einfachheit halber als Methan berechnet werden sollen, ebenfalls für die Erzeugung von elektrischer Energie ein, so können weitere 320 kWh und eine Wärmemenge von 2.200.000 kJ erzeugt werden.

Selbst bei Einsatz des als besonders ungünstig einzustufenden Tetrachlorkohlenstoffs ist, wie ersichtlich, das beschriebene Verfahren imstande, zumindest für sich selbst die erforderliche Energie zu liefern.

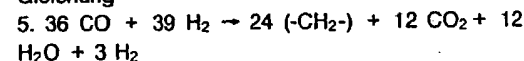
#### Ausführungsbeispiel B

Wesentlich günstiger gestaltet sich die Stoff- und Energiebilanz in dem als Fischer-Tropsch-Synthese bezeichneten Verfahrensschritt bei der Beseitigung von polychlorierten Biphenylen mit beispielsweise der Summenformel  $\text{C}_{12}\text{H}_6\text{Cl}_4$ .

Geht man von der Reaktionsgleichung



für die Zersetzungsreaktion aus, so erhält man durch die Fischer-Tropsch-Synthese, die nach der Gleichung



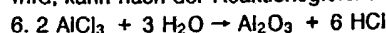
verläuft, pro Tonne des genannten PCP etwa 380 kg Kohlenwasserstoffe, wovon etwa 200 kg als Benzin gebraucht werden können und ca. 130 kg gasförmig sind. Durch Verbrennen der Gase und Nutzung des anfallenden Dampfes kann die für die Zersetzungsreaktion erforderliche Energie ohne Schwierigkeiten aufgebracht werden.

Ein weiterer Vorteil ist hierbei, daß kein zusätz-



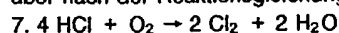
licher Kohlenstoff erforderlich ist.

Die Zersetzung des Metallchlorids, das durch Sublimation aus dem Wassergas abgeschieden wird, kann nach der Reaktionsgleichung



erfolgen.

Der gasförmige Chlorwasserstoff wird nach einem modifizierten Deacon-Verfahren, im Prinzip aber nach der Reaktionsgleichung

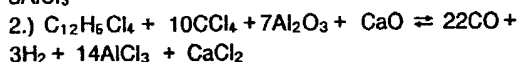
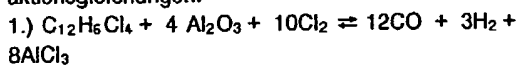


in elementares Chlor umgewandelt, das komprimiert und für industrielle Zwecke eingesetzt werden kann.

Ein modifizierter und zugleich teilweise vereinfachter Verfahrensgang nach der Erfindung bietet sich zur Energiegewinnung aus giftigen Abfallstoffen bei deren gleichzeitiger Entsorgung, wobei die Abfallstoffe insbesondere teichlorierte Kohlenwasserstoffe wie Chlophene oder Biphenyle beispielsweise entsprechend der Summenformel  $\text{C}_{12}\text{H}_5\text{Cl}_4$  und dergleichen Stoffe enthalten, durch eine Folge von Arbeitsschritten wie folgt an:

- daß der Abfall nach Maßgabe seines Gehalts an Chlor mit einer stöchiometrisch ausgewogenen Menge eines Gemisches aus Metalloxid und elektrisch leitfähigem Material wie Elektrographit bzw. Elektrodenkoks zu einem Gemenge aufbereitet wird,
- daß das Gemenge in eine beheizbare Reaktorstufe aufgegeben und darin unter Gasentwicklung aufgeheizt wird, und
- daß dem aufgeheizten Gemenge in der Reaktorstufe elementares Chlor oder gesättigte Chlorkohlenwasserstoffe in einer solchen anteiligen Menge zugesetzt werden, daß das Verhältnis von Kohlenwasserstoff-Atomen zu Chlor-Atomen etwa 1 : 2 beträgt.

Durch die Umsetzung des in einem der Reaktionsstufen vorgeschalteten Mischvorgang erzeugten Gemenges von Abfall mit einer entsprechend seinem Chlorgehalt stöchiometrisch ausgewogenen Menge an Metalloxid und elektrisch leitfähigem im wesentlichen Kohlenstoff enthaltendem Material wie Elektrographit bzw. Elektrodenkoks zu einem Gemenge und dessen Umsetzung in der beheizbaren Reaktionsstufe bei Hochtemperaturzersetzung unter gleichzeitiger Zugabe von elementarem Chlor oder gesättigten Chlorkohlenwasserstoffen wird sehr vorteilhaft ein Gasgemisch erzeugt, das im wesentlichen Kohlenmonoxid, geringe Anteile von Wasserstoff und flüchtiges Metallchlorid enthält. Die Umsetzung erfolgt beispielsweise nach folgenden Reaktionsgleichungen:



Das so entstandene Gasgemisch, welches wegen

vergleichsweise geringeren Wasserstoffgehaltes für die Durchführung der Fischer-Tropsch-Synthese weniger geeignet ist, wird nach Abscheidung des Metallchlorids verdichtet und in einem Gasbehälter gesammelt. Von dort kann es beispielsweise einem mit einem Generator gekoppelten Gasmotor zugeführt und wenigstens teilweise in elektrische Energie und Wärme umgesetzt werden.

Ein Teil dieses Produktgases kann nach dem Sammelbehälter abgezweigt und in die Reaktionsstufe rezirkuliert werden.

Der modifizierte Verfahrensgang ist sehr wirtschaftlich, insbesondere deshalb, weil zu seiner Durchführung eine vergleichsweise vereinfachte Anlage ausreichend ist.

Eine vorteilhafte Ausgestaltung des modifizierten und vereinfachten Verfahrens sieht vor, daß die Zersetzung der Abfallstoffe und deren Umsetzung bei Temperaturen zwischen  $800^\circ$  und  $1.100^\circ \text{C}$  vollzogen wird.

Hierbei wird der Reaktor und/oder das elektrisch leitfähige Material vorzugsweise induktiv beheizt.

Die induktive Beheizung eines Gemenges, welches in homogener Verteilung elektrisch leitfähige Partikel aufweist, hat den Vorteil, daß damit in der gesamten Masse des Gutes von innen heraus Wärme erzeugt wird, wodurch eine intensive thermische Zersetzung vollzogen wird.

Eine Ausgestaltung des Verfahrens sieht mit Vorteil vor, daß als Metalloxid Rotschlamm verwendet wird.

Bekanntlich ist Rotschlamm ein wirtschaftlich nicht verhüttbares Abfallprodukt, dessen Entsorgung bisher teilweise mit nicht unerheblicher Aufwendung von Kosten vorgenommen werden mußte. Wie bereits vorgängig erwähnt, kann nunmehr Rotschlamm in Verbindung mit dem erfindungsgemäßen Verfahren wirtschaftlich genutzt werden, wobei dieses Produkt in leicht trennbare Metallchloride überführt wird, die entweder als solche oder nach Umwandlung in die Oxide in verschiedenen Wirtschaftszweigen und Verfahrensgängen vorteilhaft verwendet werden können.

Wenn auch einerseits die mit der Erfindung bevorzugt vorgeschlagene Verwendung von Rotschlamm als Metalloxid zu wirtschaftlich und reaktionskonetisch sehr vorteilhaften Ergebnissen führt, so soll andererseits die Verwendung anderer Metalloxide oder Metallhydroxide ebenfalls unter die Lehre der Erfindung fallen. So können anstelle oder anteilig zum Rotschlamm Metalloxide und / oder Metallhydroxide enthaltende Stoffe wie Filterstäube, Flugaschen, Flugsande, alte Haldenberge, Galvanikschlämme und dergleichen Stoffe im Verfahren nach der Erfindung eingesetzt werden. Dies erspart gegebenenfalls eine kostanträchtige Entsorgung dieser Stoffe und eröffnet hierfür eine wirt-

schaftlich und technisch sinnvolle und somit vorteilhafte Verwendung.

Eine Ausgestaltung des Verfahrens sieht weiterhin mit Vorteil vor, daß die in die Reaktionsstufe eingetragenen Gemengestoffe darin im Fließbett von heißem Gas durchströmt werden, wobei hierfür vom verdichteten Produktgas ein Teilstrom abgezweigt und durch die Reaktionsstufe bzw. durch das Fließbett hindurchgeleitet wird.

Dabei wird mit Vorteil der abgezweigte Teilstrom des verdichteten Produktgases durch indirekten Wärmeaustausch mit aus der Reaktionsstufe abgezogenem Gas auf eine Temperatur von vorzugsweise 400° C aufgeheizt.

Hierbei wird mit Vorteil der in die Reaktionsstufe zurückgeführte Teilstrom verdichteten Produktgases mit einem solchen Produkt aus Volumen pro Zeiteinheit und Druckenergie eingeleitet, daß das Füllgut innerhalb der Reaktionsstufe zum Fließbett angeregt wird.

Bekanntlich ist die Reaktionskinetik innerhalb eines Fließbettes besonders intensiv und führt somit zu hohen Umsetzungsgraden.

Eine sehr vorteilhafte Ausgestaltung sieht hierbei vor, daß die Ausbildung des Fließbettes durch Beaufschlagen der Reaktionsstufe mit Vibrationsimpulsen, die in Richtung einer oder mehrerer Achsen wirken, unterstützt werden kann.

Eine weitere Ausgestaltung sieht vor, daß das aus der Reaktionsstufe abgezogene, außer Kohlenmonoxid und Wasserstoff noch die flüchtigen Metallchloride enthaltende heiße Gas in einer nachgeschalteten Kühlstufe gekühlt, woraufhin in einer nachgeschalteten Kondensationsstufe das Metallchlorid als Sublimat aus dem Gas ausgefällt und vorzugsweise in einer Trennstufe vom Gas getrennt und das Sublimat aus dem Prozeß ausgeschieden wird.

Und schließlich ist vorgesehen, daß das vom Metallchlorid getrennte Produktgas in einer nachgeschalteten Enstaubungsstufe nachgereinigt, sodann verdichtet und in einen Vorratsbehälter zur weiteren Verwendung vorzugsweise zum einen Teil zur Energiegewinnung und zum restlichen Teil zur Rückführung in die Reaktionsstufe verwendet wird.

Eine erfindungsgemäße Anlage zur Durchführung des in den Ansprüchen 1 bis 12 beanspruchten Verfahrens ist gekennzeichnet durch einen Aufgabeebehälter für die zu verarbeitenden Abfallstoffe mit nachgeschaltetem Förderer, vorzugsweise einer Pumpe, einem nachgeschalteten Verdampfer, einem nachgeschalteten und vorzugsweise induktiv beheizbaren Reaktor, einem nachgeschalteten als Kühler ausgebildeten Wärmeaustauscher mit zugeordnetem Sublimator, einem nachgeschalteten Gasfilter, Gasometer, Verdichter und einer Synthesanlage mit zugeordneten Trennsäulen und Lagertanks.

Ein weiterer erfindungsgemäßer Vorschlag zur Ausgestaltung der Anlage geht dahin, daß dem Reaktor eine Pumpe sowie eine Wasserverdampfer- und Dampfüberhitzereinheit zugeordnet sind.

Fernerhin ist die Trennsäule am Kopfende mit einer Zuleitung zu einem Gasometer verbunden, an den ein Gasmotor mit einem Generator angeschlossen ist.

Und schließlich ist in vorteilhafter Ausgestaltung an den Sublimator ein Regenerator und Oxidator mit Tank angeschlossen.

Eine im Prinzip ähnliche, teilweise vereinfachte und zur Durchführung des modifizierten Verfahrensganges nach den Ansprüchen 13 bis 22 in besonderer Weise ausgebildete Anlage mit einem Aufgabeebehälter für die zu verarbeitenden Abfallstoffe, insbesondere teilchlorierte Kohlenwasserstoffe und einem nachgeschalteten Förderer, vorzugsweise einer Pumpe, ist gekennzeichnet durch einen Mischbehälter mit Mitteln zur dosierbaren Aufgabe dieser Abfallstoffe, ferner mit Mitteln zur dosierbaren Aufgabe eines Gemisches aus Metalloxid und elektrisch leitendem Material wie Elektrographit oder Elektrodenkoks mit einem nachgeschalteten und vorzugsweise induktiv beheizbaren Reaktor mit Mitteln zur dosierbaren Aufgabe des im Mischbehälter hergestellten Gemenges, sowie mit Mitteln zur dosierbaren Aufgabe von elementarem Chlor bzw. gesättigten Chlorkohlenwasserstoffen, und mit Mitteln zur dosierbaren Einleitung von Wasserdampf, sowie mit Einrichtungen zur Erzeugung eines Fließbettes, in welches eine Produktgasleitung einmündet.

Eine Ausgestaltung der Anlage sieht vor, daß dem Reaktor ein indirekter Gas/Gas-Wärmeaustauscher nachgeschaltet ist, mit einem weiterhin nachgeschalteten Kondensator/Sublimator mit Mitteln zum Austrag von abgeschiedenem Metallchlorid, wobei diesem jeweils ein Gasfilter, Verdichter und Gasbehälter nachgeschaltet sind.

Eine vorteilhafte Ausgestaltung der Anlage sieht vor, daß der Reaktor in einem Sicherheitsbehälter angeordnet bzw. von diesem umgeben ist.

Weiterhin ist eine vorteilhafte Kreislaufführung von Wärmeströmen innerhalb der Anlage dadurch erreichbar, daß der Gasbehälter über eine Produktgasleitung an eine der Wärmeaustauschseiten des Wärmeaustauschers angeschlossen ist, und daß die andere Wärmeaustauschseite des Wärmeaustauschers über eine Leitung an den Gasaustritt des Reaktors angeschlossen ist.

Auf diese Weise wird ein sehr vorteilhafter Wärmeaustausch zwischen dem mit hoher Temperatur aus dem Reaktor austretenden Gas und dem in das Fließbett des Reaktors zurück geführten Teilstrom von Produktgas vollzogen. Durch diesen vorteilhaften Wärmeaustausch wird dem aus dem

Reaktor austretenden hochtemperierten Gas Wärme entzogen, es wird gekühlt, und das in den Reaktor bzw. das Fließbett als Reaktionsgas eingeleitete Produktgas auf wenigstens 400° C vorgewärmt.

Eine Ausgestaltung der Anlage sieht weiter vor, daß der Gasbehälter über eine weitere Produktgasleitung zur Energiegewinnung an eine Brennkraftmaschine wie Gasmotor oder Gasturbine angeschlossen ist, der einen Generator antreibt.

Dabei kann diese Brennkraftmaschine brennluftseitig an eine Einrichtung oder Quelle zur Lieferung von einem Luft/Sauerstoff-Gemisch oder technischem Sauerstoff angeschlossen sein, um anstelle reiner Brennluft mit Sauerstoff-Gemisch oder Sauerstoff betrieben zu werden. Das hierbei anfallende Abgas enthält dann vergleichsweise weniger Stickstoff- oder Stickoxid-Anteile und vergleichsweise mehr CO<sub>2</sub>-Anteile. Dieses so mit Kohlenstoff angereicherte Abgas wird vorzugsweise in das Fließbett des Reaktors rezirkuliert und intensiviert mit Vorteil die Reaktionskinematik der ablaufenden Reaktionen.

Und schließlich sieht eine erfindungswesentliche Ausgestaltung der Anlage vor, daß der Reaktor Mittel zur Schwingungserregung aufweist.

Die Erfindung wird in einer schematischen Darstellung von Blockschaltbildern in jeweils einer bevorzugten Ausführungsform gezeigt, wobei aus den Blockschaltbildern weitere vorteilhafte Einzelheiten des erfindungsgemäßen Verfahrens und der erfindungsgemäßen Anlage entnehmbar sind.

Die Zeichnungen zeigen im einzelnen:

Figur 1 eine Anlage zur Durchführung des Verfahrensganges entsprechend den Ansprüchen 1 bis 12, in der rein schematischen Darstellung eines Blockschaltbildes,

Figur 2 eine Anlage zur Durchführung des modifizierten und vereinfachten Verfahrensganges entsprechend den Ansprüchen 13 bis 21, ebenfalls in rein schematischer Darstellung in Form eines Blockschaltbildes.

Zur Durchführung des Verfahrens entsprechend den Ansprüchen 1 bis 12 zur Energiegewinnung aus giftigen Abfallstoffen bei deren gleichzeitiger Entsorgung, wobei die Abfallstoffe zumindest erhebliche Anteile von substituierten Kohlenwasserstoffen aufweisen, wie sie beispielsweise als Chlorverbindungen bzw. Chlorkohlenwasserstoffe vorliegen, wird gemäß Blockschaltbild in der Figur 1 der in einem Behälter 1 aufbewahrte beispielsweise flüssige und giftige Abfallstoff mit Hilfe der Pumpe 2 über den Durchflußmesser 3 in den Verdampfer 4 gepumpt, in welchem er auf Siedetemperatur erhitzt wird. Der aus dem Verdampfer ausströmende Dampf gelangt in den mit Kohlenstoff und einem schwer verhüttbaren Metalloxid gefüllten, in-

duktiv beheizten Reaktor 5, in dem bei einer Temperatur zwischen 800° und 1.000° C die Zersetzung und die Bildung von Kohlenmonoxid sowie des flüchtigen Metallchlorids stattfindet.

Gleichzeitig wird mit Hilfe der Pumpe 6 über den Durchflußmesser 7 und den Wasserverdampfer und Dampfüberhitzer 8 soviel Wasserdampf in den Reaktor 5 eingeblasen, daß entsprechend einer vorherigen stöchiometrischen Rechnung ein bestimmtes, aus Kohlenmonoxid und Wasserstoff bestehendes Gasgemisch erzeugt wird.

Das Gasgemisch gelangt zusammen mit dem flüchtigen Metallchlorid über den Wärmeaustauscher 9 zu dem Sublimator 10, in dem sich das Metallchlorid in fester Form niederschlägt.

Über einen nachgeschalteten Filter 11 gelangt das Wassergas, CO und H<sub>2</sub>, in den Gasometer 12 und wird von dort über den Verdichter 13 und den Erhitzer 14, der nur zu Beginn des Prozesses benutzt wird, in die Synthese-Anlage 15 eingeleitet, in der die Bildung nutzbarer Kohlenwasserstoffe erfolgt. Mit H<sub>2</sub>O ist das zugeführte Kühlwasser bezeichnet. Das die Synthese-Anlage verlassende gasförmige Produkt wird in den Trennsäulen 16 in die verschiedenen Fraktionen aufgespalten und in den Lagertanks 17 gesammelt.

Die am Kopf der Trennsäulen 16 austretenden permanent gasförmigen Kohlenwasserstoffe werden im Gasometer 18 bevorratet und strömen von dort zu einem Gasmotor 19, der mit einem Generator 20 gekoppelt ist.

Der aus der Fischer-Tropsch-Anlage 15 ausströmende heiße Dampf, der aus dem erforderlichen Kühlwasser entsteht, gelangt über den Dampfüberhitzer 21 zu einer Dampfkraftmaschine 22, die ebenfalls mit dem Generator 20 gekoppelt ist.

Das im Sublimator anfallende Metallchlorid wird im Regenerator 23 in Metalloxid und Chlorwasserstoff umgewandelt. Der Chlorwasserstoff wird im Oxidator 24 nach dem Deacon-Prozeß zu Chlor oxidiert und nach Verdichtung in dem Verdichter 25 in den Tanks 26 gelagert.

Das zurückgewonnene Metalloxid wird wieder dem Reaktor 5 zugeführt.

Zur Durchführung des modifizierten und vereinfachten Verfahrens zur Energiegewinnung aus giftigen Abfallstoffen bei deren gleichzeitiger Entsorgung, wobei die Abfallstoffe insbesondere teilchlorierte Kohlenwasserstoffe wie Chlophene und dergleichen Stoffe enthalten, entsprechend dem Verfahrensgang nach den Ansprüchen 13 bis 21, wird der in einem Behälter 41 als Flüssigkeit mit oder ohne Anteile von Feststoffpartikeln aufbewahrte giftige Abfall mit Hilfe eines Förderers 42, beispielsweise einer Pumpe oder eines Schneckenförderers, über das Dosierorgan 43 in den Mischbehälter 40 aufgegeben. Weiterhin wird in diesem Mischbe-

hälter 40 nach Maßgabe des Gehaltes der Abfallstoffe an Chlor eine stöchiometrisch ausgewogene Menge eines Gemisches aus Metalloxid 68 und elektrisch leitfähigem Material 69/73 wie Elektrographit bzw. Elektrodenkoks aufgegeben und mit den Abfallstoffen durch das Rührwerk 70 im Mischbehälter 40 zu einem homogenen Gemenge aufbereitet. Fallweise kann diesem Gemenge Wasserdampf zugegeben werden, welcher durch die Pumpe 49, den Verdampfer 50 und die Dosiereinrichtung 51 in den Mischer 40 eingetragen wird.

Das so im Mischvorgang durch das Mischorgan 70 zum Gemenge aufbereitete Gut wird sodann durch eine Austragsschleuse 71 kontinuierlich oder chargenweise in den Förderer 53 ausgetragen und von diesem dem Reaktor 52 aufgegeben. Dieser ist an seinem unteren Ende mit Mitteln 54 zur Erzeugung eines Fließbettes ausgebildet. Weiterhin ist der Reaktor von einem Sicherheitsbehälter 62 umgeben. Das aus dem Reaktor 52 und Sicherheitsbehälter 62 bestehende System kann darüberhinaus schwingungsfähig gelagert sein und Schwingungserreger 68 aufweisen, welche Schwingungen vorzugsweise in zwei Schwingungsebenen erzeugen. Vom Reaktor 52 führt eine Gasaustrittsleitung 64 zu dem indirekten Gas/Gas-Wärmeaustauscher 56. Dieser ist einerseits durchströmt von heißem, aus dem Reaktor 52 austretendem Gas, welches mit einer Temperatur zwischen 800° und 1.100° C anfällt. Im Gegenstrom dazu wird durch den Wärmeaustauscher 56 ein aus dem gereinigten, gekühlten und verdichteten Produktgas abgezweigter Teilstrom mit der Leitung 63 dem Wärmeaustauscher 56 zugeführt und nach Erwärmung auf etwa 400° C durch Wärmeaustausch mit dem Reaktorgas von unten her mit der Leitung 55 in den Reaktor 52 bzw. durch das Fließbett 54 hindurch geleitet.

Das nach Kühlung durch Wärmeabgabe an den Teilgasstrom aus dem Wärmeaustauscher 56 austretende Reaktorgas wird in den Kondensator bzw. Sublimator 57 eingeleitet, dort unter die Kondensationstemperatur der zunächst flüchtigen Metallchloride abgekühlt und diese darin niedergeschlagen. Die staubförmig anfallenden Metallchloride werden sodann durch die Austragschleuse 58 zunächst aus dem Prozeß ausgeschieden. Sie können, wie das vorgängig bereits beschrieben ist, beispielsweise durch einen modifizierten Deacon-Prozeß wieder in Metalloxide überführt und erneut in den Verfahrensgang eingeschleust werden.

Das von Metallchloriden gereinigte Reaktorgas wird in einem Staubfilter 59 nachgereinigt, in einem Verdichter 60 verdichtet und sodann in den Behälter 61 zur weiteren Verwendung eingeleitet. Aus diesem wird einerseits das zur Aufrechterhaltung des Fließbettes 54 im Reaktor 52 benötigte Reaktionsgas entnommen, wogegen der hierfür nicht

benötigte Überschuß an Gas über die Leitung 65 und das Drosselorgan 72 einem Gasmotor 66 als Brennstoff zugeführt wird, der seinerseits den Generator 67 antreibt. Auf diese Weise wird das nicht rezirkulierte Produktgas zur Energiegewinnung herangezogen.

Beim Betrieb dieses Gasmotors 66 mit Luft/Sauerstoff-Gemisch oder Sauerstoff anstelle von Brennluft ergeben sich darüberhinaus die vorgängig erläuterten Vorteile bei Rezirkulation des Abgases in den Reaktor bzw. in das Fließbett.

Das beschriebene modifizierte Verfahren gemäß Stammbaum in Figur 2 sowie entsprechend den Ansprüchen 13 bis 21 ist ersichtlicherweise sehr unkompliziert, hocheffizient in der Umsetzung und erfordert eine erheblich vereinfachte Ausführung der Anlage. Außerdem ist das Verfahren geeignet, die für den Prozeß benötigte autotherme Energie selbst zu liefern und darüberhinaus noch durch Überschuß seiner Wärmebilanz nutzbare Energie zu erzeugen. Entsprechend dem

#### Ausführungsbeispiel C

wird zur Energiegewinnung aus giftigen Abfallstoffen bei deren gleichzeitiger Entsorgung, wobei die Abfallstoffe insbesondere teilchlorierte Kohlenwasserstoffe wie Clophene oder Biphenyle und dergleichen Stoffe nach der Summenformel  $C_{12}H_6Cl_4$  enthalten, entweder die Zugabe von Chlorgas in den für die Umsetzung vorgesehenen Reaktor vorgeschlagen, oder die Vermischung mit vollständig chlorierten Kohlenwasserstoffen. Dadurch ergeben sich beispielsweise folgende Reaktionsgleichungen:

- 1.)  $C_{12}H_6Cl_4 + 4Al_2O_3 + 10Cl_2 \rightleftharpoons 12CO + 3H_2 + 8AlCl_3$
- 2.)  $C_{12}H_6Cl_4 + 10CCl_4 + 7Al_2O_3 + CaO \rightleftharpoons 22CO + 3H_2 + 14AlCl_3 + CaCl_2$

Das entstehende Gasgemisch, welches beim vorgeschlagenen vereinfachten Verfahrensgang wegen seines geringeren Wasserstoffgehaltes für die Fischer-Tropsch-Synthese wirtschaftlich nicht geeignet ist, wird nach Abscheidung des Metallchlorids verdichtet und in einem Gasometer gesammelt. Von dort wird es einem mit einem Generator gekoppelten Gasmotor zugeführt und in elektrische Energie und Wärme umgesetzt.

Zur Durchführung des Verfahrens wird vorzugsweise ein Gemisch von Rotschlamm und einem elektrisch leitenden, im wesentlichen Kohlenstoff enthaltenden Stoff, vorzugsweise Elektrographit oder Elektrodenkoks in pulverförmigem Zustand mit den Abfällen zu einem Gemenge vermischt und mit einer geeigneten Fördereinrichtung in den vorzugsweise induktiv beheizten Reaktor eingetragen.

Gleichzeitig wird darin ein geeignet dosiertes

Clorgasvolumen sowie ein Gasgemisch aus Kohlenmonoxid und Wasserstoff in solcher Menge ein- geleitet, daß sich innerhalb des Reaktors zusammen mit dem eingetragenen Feststoff, dem Gemisch aus Rotschlamm und Elektrographit bzw. Elektrodenkoks, ein Fließbett ausbildet.

Das aus Kohlenmonoxid und Wasserstoff bestehende Gasgemisch wird während des Betriebes der Anlage den nach Gleichung 1.) bzw. 2.) gebildeten Gasstrom hinter dem Gasometer entnommen und vorzugsweise durch das aus dem Reaktor entweichende heiße Gas auf etwa 400° C aufgeheizt. Hierdurch und durch die vorzugsweise induktive Beheizung des Reaktors wird erreicht, daß beim Kontakt des Gases mit dem Rotschlamm-Elektrographit-Abfallmenge die als Abfall eingebrachten ungesättigten Chlorkohlenwasserstoffe in die Dampf- bzw. Gasphase übergehen. Die Ausbildung des Fließbettes kann dadurch unterstützt werden, daß der Reaktor mit Hilfe einer Vibrationseinrichtung Impulse empfängt, die in Richtung einer oder mehrerer seiner Achsen wirken.

Der in den Prozeß eingetragene Rotschlamm, welcher durch die Reaktion mit dem chlorhaltigen Abfällen zu Aluminium-Chlorid umgesetzt wurde, kann entweder als solches verworfen werden oder durch Umwandlung in Metalloxid mit einem hierfür geeigneten, nicht zur Erfindung gehörenden Prozeß einer anderweitigen wirtschaftlichen Verwendung zugeführt werden.

Gleiche Vorteile gelten für die Verwendung ganz oder teilweise anderer Metalloxide enthaltende Stoffe wie Filterstäube, Flugaschen, Flugsande, Haldenberge, Galvanikschlämme und ähnlicher Stoffe. Zugleich wird deren Entsorgung von den bisher hierfür bestehenden Schwierigkeiten, Kosten und Gefahren für die Umwelt entlastet.

#### Ansprüche

1. Verfahren zur Energiegewinnung aus giftigen Abfallstoffen bei deren gleichzeitiger Entsorgung, wobei die Abfallstoffe zumindest erhebliche Anteile von substituierten Kohlenwasserstoffen aufweisen, wie sie beispielsweise als Chlorverbindungen bzw. Chlorkohlenwasserstoffe der Formeln  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{C}_2\text{H}_2\text{Cl}_4$ , PCB, PVC, Polyvinylidenchlorid etc. vorliegen, **dadurch gekennzeichnet**, daß der Abfallstoff in einem beheizbaren Reaktor in Anwesenheit eines schwer verhüttbaren Metalloxides und eines elektrisch leitfähigen Materials, beispielsweise Elektrodenkoks oder Elektrographit, sowie im Kontakt mit Wasserdampf thermisch zersetzt wird, wobei eine dem Chlorgehalt der Abfallstoffe entsprechende Metalloxidmenge in flüchtiges Metallchlorid sowie ein Anteil freier Kohlenstoffs in Kohlenmonoxid und ein mit dem Metalloxid nicht rea-

gierender Anteil des Kohlenstoffs mit Hilfe einer stöchiometrischen Menge Wasserdampf zu Wassergas,  $\text{CO} + \text{H}_2$ , umgesetzt wird.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet**, daß die Zersetzung der Abfallstoffe und deren Umsetzung bei Temperaturen zwischen 800 und 1100° C vollzogen wird.

3. Verfahren nach Anspruch 1 oder 2, **dadurch gekennzeichnet**, daß der Reaktor und/oder das elektrisch leitfähige Material induktiv beheizt werden.

4. Verfahren nach einem der Ansprüche 1 bis 3, **dadurch gekennzeichnet**, daß das im Reaktor entstandene Wassergas,  $\text{CO} + \text{H}_2$ , durch anschließende Fischer-Tropsch-Synthese in Kohlenwasserstoffen umgewandelt wird und diese vorzugsweise zur Energieerzeugung verwendet werden.

5. Verfahren nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet**, daß die bei der Umsetzung entstehenden gasförmigen Kohlenwasserstoffe zur Deckung des Energiebedarfes in den verschiedenen Verfahrensstufen herangezogen werden.

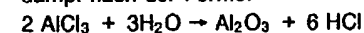
6. Verfahren nach Anspruch 1, **dadurch gekennzeichnet**, daß als schwer verhüttbares Metalloxid  $\text{Al}_2\text{O}_3$  oder  $\text{TiO}_2$  verwendet wird.

7. Verfahren nach Anspruch 1 und 6, **dadurch gekennzeichnet**, daß zusätzlich und/oder anstelle von  $\text{Al}_2\text{O}_3$  oder  $\text{TiO}_2$  ein Gemenge von schwer und weniger schwer verhüttbaren Metalloxiden verwendet wird, bzw. daß zusätzlich und/oder anstelle eines oder mehrerer dieser schwer oder weniger schwer verhüttbaren Metalloxide Stoffe eingesetzt werden, in welchen Metalloxide oder Metallhydroxide enthalten sind, wie Filterstäube, Flugaschen, Flugsande, Haldenberge, Galvanikschlämme oder dergleichen Stoffgemische.

8. Verfahren nach Anspruch 1, **dadurch gekennzeichnet**, daß als leitfähiges Material ein Metall verwendet wird.

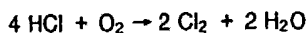
9. Verfahren nach Anspruch 1, **dadurch gekennzeichnet**, daß das im Reaktor erzeugte flüchtige Metallchlorid aus dem Gas durch Sublimation bzw. Kondensation und nachfolgende Trennung abgeschieden wird.

10. Verfahren nach den Ansprüchen 1 und 9, **dadurch gekennzeichnet**, daß das abgeschiedene Metallchlorid durch Umsetzung mit Wasserdampf nach der Formel



wieder zu Metalloxid umgesetzt und dieses erneut in den Prozeß zurückgeführt wird.

11. Verfahren nach Anspruch 1 und 10, **dadurch gekennzeichnet**, daß das bei der Umsetzung von Metallchlorid in Metalloxid entstandene Chlorwasserstoffgas  $\text{HCl}$  durch Umsetzung mit Sauerstoff beispielsweise nach der Formel



in elementares Chlor und Wasserdampf zerlegt wird.

12. Verfahren nach Anspruch 1 und 4, **dadurch gekennzeichnet**, daß bei der Kühlung der Fischer-Tropsch-Synthesestufe anfallender Wasserdampf ganz oder zumindest teilweise zur Energiegewinnung verwendet wird.

13. Verfahren zur Energiegewinnung aus giftigen Abfallstoffen bei deren gleichzeitiger Entsorgung, insbesondere in einem für teilchlorierte Kohlenwasserstoffe wie Chlrophene und dergleichen enthaltende Abfallstoffe in besonderer Weise ausgebildeten bzw. abgewandelten Verfahrensgang, **gekennzeichnet durch** eine Folge von Arbeitsschritten:

- daß der Abfall nach Maßgabe seines Gehalts an Chlor mit einer stöchiometrisch ausgewogenen Menge eines Gemisches aus Metalloxid und elektrisch leitfähigem Material wie Elektrographit bzw. Elektrodenkoks zu einem Gemenge aufbereitet wird,

- daß das Gemenge in eine beheizbare Reaktorstufe aufgegeben und darin unter Gasentwicklung aufgeheizt wird, und

- daß dem aufgeheizten Gemenge in der Reaktorstufe elementares Chlor oder gesättigte Chlorkohlenwasserstoffe in einer solchen anteiligen Menge zugesetzt werden, daß das Verhältnis von Kohlenwasserstoff-Atomen zu Chlor-Atomen etwa 1:2 beträgt.

14. Verfahren nach Anspruch 13, **dadurch gekennzeichnet**, daß die zum weitgehend homogenen Gemenge aufbereiteten Stoffkomponenten kontinuierlich in die Reaktorstufe eingetragen und darin im Durchlauf auf Temperaturen zwischen 800 °C und 1100 °C aufgeheizt werden.

15. Verfahren nach Anspruch 13, **dadurch gekennzeichnet**, daß die in die Reaktionsstufe eingetragenen Gemengestoffe darin im Fließbett von heißem Gas durchströmt werden, wobei hierfür vom verdichteten Produktgas ein Teilstrom abgezweigt und durch die Reaktionsstufe bzw. durch das Fließbett hindurch geleitet wird.

16. Verfahren nach Anspruch 13, **dadurch gekennzeichnet**, daß der abgezweigte Teilstrom des verdichteten Produktgases durch indirekten Wärmeaustausch mit aus der Reaktionsstufe abgezogenem Gas auf eine Temperatur von vorzugsweise 400 °C aufgeheizt wird.

17. Verfahren nach Anspruch 13, **dadurch gekennzeichnet**, daß der in die Reaktionsstufe zurückgeführte Teilstrom verdichteten Produktgases mit einem solchen Produkt aus Volumen pro Zeiteinheit und Druckenergie eingeleitet wird, daß das Füllgut innerhalb der Reaktionsstufe zum Fließbett angeregt wird.

18. Verfahren nach Anspruch 1 sowie 13 bis 17, **dadurch gekennzeichnet**, daß bei der Energiegewinnung mittels Produktgas beispielsweise in einer Brennkraftmaschine anfallendes Abgas zur Unterstützung der Fließbettauflösung in den Reaktor zurückgeführt wird.

19. Verfahren nach Anspruch 18, **dadurch gekennzeichnet**, daß die zur Energiegewinnung mit Produktgas betriebene Brennkraftmaschine anstelle von Brennluft mit einem Luft/Sauerstoff-Gemisch oder zumindest teilweise mit Sauerstoff betrieben wird und das Abgas vergleichsweise geringere Anteile an Stickoxiden und vergleichsweise höhere Anteile an CO<sub>2</sub> enthält und somit bei der Rezirkulation in das Fließbett der Reaktorstufe die Reaktionskinetik der Stoffumsetzung durch den erhöhten Gehalt an Kohlenstoff intensiviert.

20. Verfahren nach einem der Ansprüche 1 sowie 13 bis 19, **dadurch gekennzeichnet**, daß die Ausbildung des Fließbettes durch Beaufschlagen der Reaktionsstufe mit Vibrationsimpulsen, die in Richtung einer oder mehrerer Achsen wirken, unterstützt wird.

21. Verfahren nach Anspruch 13, **dadurch gekennzeichnet**, daß das aus der Reaktionsstufe abgezogene, außer Kohlenmonoxid und Wasserstoff noch die flüchtigen Metallchloride enthaltende heiße Gas in einer nachgeschalteten Kühlstufe gekühlt, woraufhin in einer nachgeschalteten Kondensationsstufe das Metallchlorid als Sublimat aus dem Gas ausgefällt und vorzugsweise in einer Trennstufe vom Gas getrennt und das Sublimat aus dem Prozeß ausgeschieden wird.

22. Verfahren nach einem der Ansprüche 13 bis 21, **dadurch gekennzeichnet**, daß das vom Metallchlorid getrennte Produktgas in einer nachgeschalteten Entstaubungsstufe nachgereinigt, sodann verdichtet und in eine Vorratsbehälter zur weiteren Verwendung eingeleitet und zum einen Teil zur Energiegewinnung und zum restlichen Teil zur Rückführung in die Reaktionsstufe verwendet wird.

23. Anlage zur Durchführung des Verfahrens nach einem oder mehreren der Ansprüche 1 bis 12, **gekennzeichnet durch** einen Aufgabebehälter (1) für die zu verarbeitenden Abfallstoffe mit nachgeschaltetem Förderer, vorzugsweise einer Pumpe (2), einem nachgeschalteten Verdampfer (4), einem nachgeschalteten und vorzugsweise induktiv beheizbaren Reaktor (5), einem nachgeschalteten als Kühler ausgebildeten Wärmeaustauscher (9) mit zugeordnetem Sublimator (10), einem nachgeschalteten Gasfilter (11), Gasometer (12), Verdichter (13) und einer Syntheseanlage (15) mit zugeordneten Trennsäulen (16) und Lagertanks (17).

24. Anlage nach Anspruch 23, **dadurch gekennzeichnet**, daß dem Reaktor (5) eine Pumpe (6) sowie eine Wasserverdampfer- und Dampfüberhitzereinheit (8) zugeordnet sind.

25. Anlage nach Anspruch 23, **dadurch gekennzeichnet**, daß die Trennsäule (17) am Kopfende mit einer Zuleitung zu einem Gasometer (18) verbunden ist, an den ein Gasmotor (22) mit einem Generator (20) angeschlossen ist.

26. Anlage nach Anspruch 23, **dadurch gekennzeichnet**, daß an den Sublimator (10) ein Regenerator (13) und Oxidator (24) mit Tank (26) angeschlossen ist (Figur 1).

27. Anlage zur Durchführung des modifizierten Verfahrens nach den Ansprüchen 13 bis 22, mit einem Aufnahmebehälter für die zu verarbeitenden Abfallstoffe, insbesondere teilchlorierte Kohlenwasserstoffe wie Chlophenone bzw. Chlorphenyle, und einem nachgeschalteten Förderer, vorzugsweise einer Pumpe, **gekennzeichnet durch** einen Mischbehälter (40) mit Mitteln (41, 42, 43) zur dosierbaren Aufgabe der Abfallstoffe, ferner mit Mitteln (45) zur dosierbaren Aufgabe eines Gemisches aus Metalloxid und elektrisch leitendem Material wie Elektrographit oder Elektrodenkoks mit einem nachgeschalteten und vorzugsweise induktiv beheizbaren Reaktor (52) mit Mitteln (53) zur dosierbaren Aufgabe des im Mischbehälter (40) hergestellten Gemenges sowie mit Mitteln (46, 47, 48) zur dosierbaren Aufgabe von elementarem Chlor bzw. gesättigten Chlorwasserstoffen, und mit Mitteln (49, 50, 51) zur dosierbaren Einleitung von Wasserdampf, sowie mit einer Einrichtung bzw. Ausbildung zur Erzeugung eines Fließbettes (54), in welches eine Produktgas-Zweigleitung (63,55) einmündet.

28. Anlage nach Anspruch 27, **dadurch gekennzeichnet**, daß dem Reaktor (52) ein indirekter Gas/Gas-Wärmeaustauscher (56) nachgeschaltet ist, mit einem diesem nachgeschalteten Sublimator (57) mit Mitteln (58) zum Austrag von Metallchlorid, und diesem jeweils ein Gasfilter (59), Verdichter (60) und Gasbehälter (61) nachgeschaltet sind.

29. Anlage nach dem Anspruch 27, **dadurch gekennzeichnet**, daß der Reaktor (52) in einem Sicherheitsbehälter (62) angeordnet bzw. von diesem umgeben ist.

30. Anlage nach Anspruch 27, **dadurch gekennzeichnet**, daß der Gasbehälter (61) über eine Produktgasleitung (63) an eine der Wärmeaustauschseiten des Wärmeaustauschers (56) angeschlossen ist.

31. Anlage nach Anspruch 27, **dadurch gekennzeichnet**, daß die andere Wärmeaustauschseite des Wärmeaustauschers (56) über eine Leitung (64) an den Gasaustritt des Reaktors (52) angeschlossen ist.

32. Anlage nach Anspruch 27, **dadurch gekennzeichnet**, daß der Gasbehälter (61) über eine weitere Produktgasleitung (65) zur Energiegewinnung an eine Brennkraftmaschine wie Gasmotor oder Gasturbine (66) angeschlossen ist, welche einen Generator (67) antreibt.

33. Anlage nach Anspruch 32, **dadurch gekennzeichnet**, daß die Brennkraftmaschine (66) zur Brennstoffzufuhr einerseits an die Produktgasleitung (64) und zur Sauerstoffzufuhr andererseits über eine (nicht dargestellte) Leitung an eine Luft und/oder Luftsauerstoffgemisch und/oder Sauerstoff liefernde Einrichtung bzw. Quelle angeschlossen ist.

34. Anlage nach Anspruch 22 und 27, **dadurch gekennzeichnet**, daß der Reaktor (52) Mittel (68) zur Schwingungserregung aufweist.

FIG.1

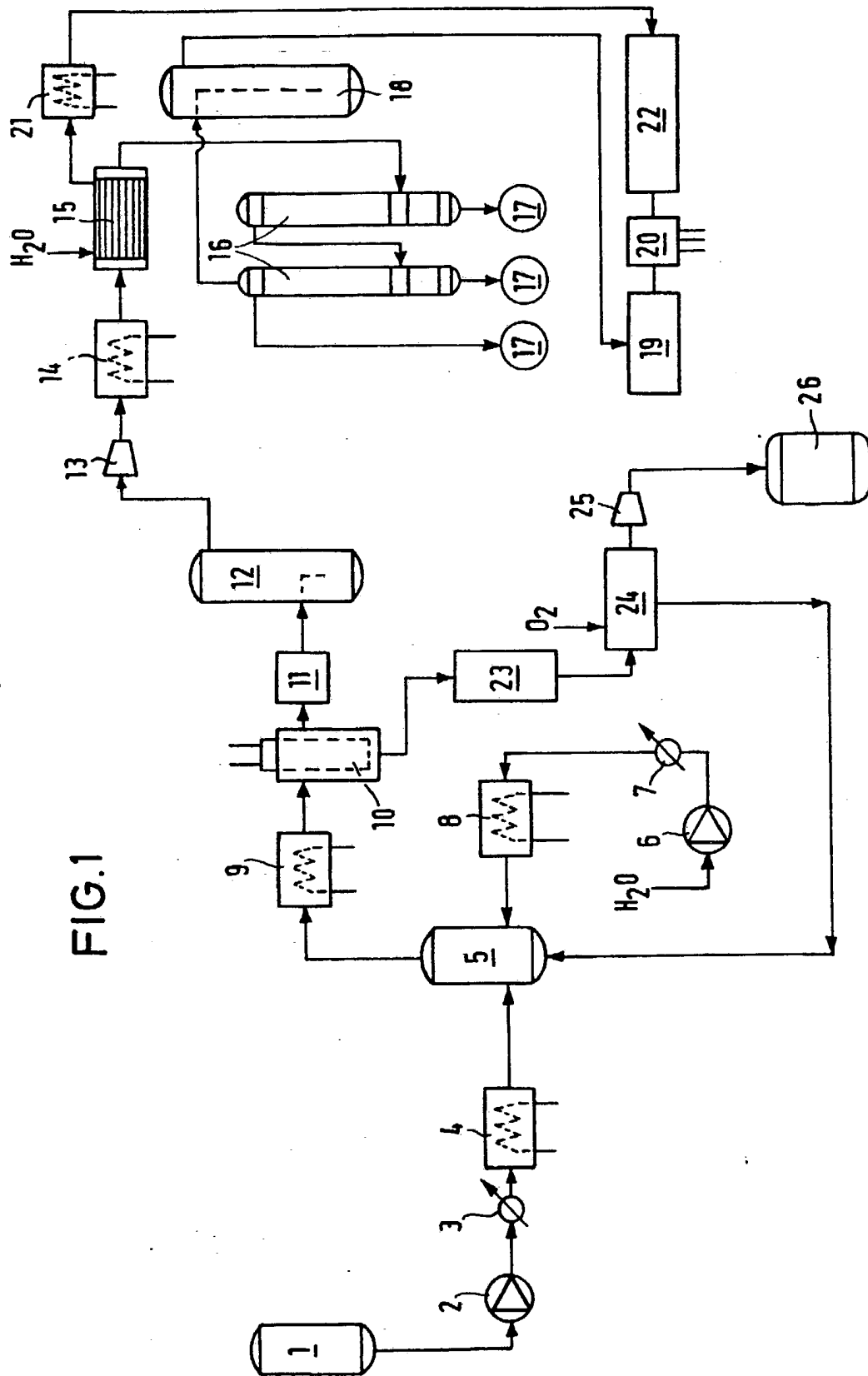
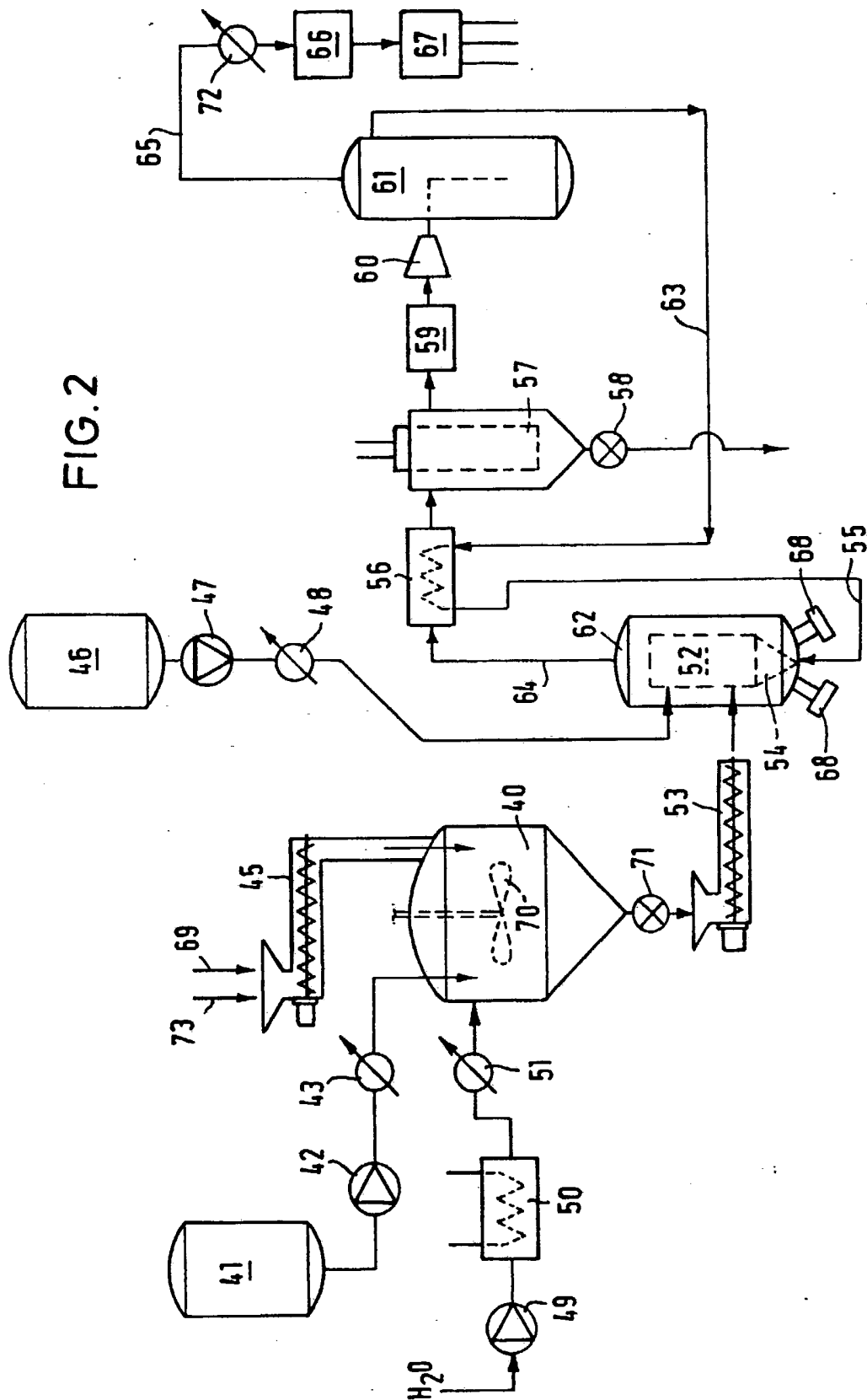




FIG. 2





Europäisches  
Patentamt

# EUROPÄISCHER RECHERCHENBERICHT

Nummer der Anmeldung

EP 87 10 7552

EINSCHLÄGIGE DOKUMENTE			
Kategorie	Kennzeichnung des Dokuments mit Angabe, soweit erforderlich, der maßgeblichen Teile	Betrifft Anspruch	KLASSIFIKATION DER ANMELDUNG (Int. Cl.4)
L	DE-A-3 640 573 (F. SUPPAN) * Insgesamt * & DE-A-3 542 092 ---	1-34	A 62 D 3/00
A	DE-A-3 313 889 (M. von AHN) * Ansprüche; Seite 7, Zeile 6 - Seite 10, Zeile 6 * ---	1-12	
A	WO-A-8 602 847 (USS ENGINEERS AND CONSULTANTS) * Seite 4, Zeilen 2-15; Seite 22, Zeile 18 - Seite 23, Zeile 33; Ansprüche * ---	1-12	
A	US-A-4 435 379 (R.S. OLSON et al.) * Spalte 2, Zeile 48 - Spalte 3, Zeile 22; Ansprüche * ---	1-34	
A	US-A-4 587 116 (D.A. LIVINGSTONE et al.) * Insgesamt * ---	1-34	
A	DE-B-2 311 213 (TH. GOLDSCHMIDT AG) * Insgesamt * -----	1-34	RECHERCHIERTE SACHGEBIETE (Int. Cl.4)  A 62 D
Der vorliegende Recherchenbericht wurde für alle Patentansprüche erstellt			
Recherchenort DEN HAAG		Abschlußdatum der Recherche 29-02-1988	Prüfer FLETCHER A.S.
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